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EDITED BY

IRA REMSEN

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY.

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# AMERICAN CHEMICAL JOURNAL.

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## THE ACTION OF NITRILES ON ORGANIC ACIDS.

BY CHARLES E. COLBY AND FRANK D. DODGE.

Two years since, in attempting to prepare some dibenzamide, we tried several methods, among which was one founded upon the reaction of Gautier,<sup>1</sup> by which he produced diacetamide on heating acetonitrile and acetic acid together in a sealed tube. Accordingly we heated equal molecules of benzonitrile and benzoic acid at 200° for four hours. Dibenzamide was formed, but the yield was small. It occurred to us that it might be well to apply the reaction to other nitriles and other acids, and we therefore experimented with a number of nitriles and acids and have obtained some remarkable results.

Gautier's experiments are described in full in the *Comptes Rendus*, 1868, Vol. 67, page 1255. According to his account, formonitrile and acetic acid produce acetamide; acetonitrile and acetic acid give diacetamide; and propionitrile and acetic acid give a mixture of triacetodiamide and diacetopropionamide. We have thought it worth while to repeat the last two of these experiments, and our results were in one case the same as, and in the other case different from, Gautier's.

Before describing our experiments in detail, it is well to state that we first made sure of the purity of our materials. The nitriles were freshly distilled over phosphorus pentoxide, and the acids were ascertained to be free from water. Equal molecules of nitrile

<sup>1</sup> *Ztschr. Chem.*, 1869, 127.

and acid were heated in a sealed tube. In several cases from three to five drops of acetic anhydride were also added to the tube, and we think the yield of product was thereby increased. After heating, a diminished pressure was observed in every case on opening the tube. The contents of the tubes were generally evaporated to dryness on a water-bath, when the uncombined nitrile or acid present was easily volatile; or were washed with dilute sodium carbonate solution, when aromatic acids were to be removed. Uncombined aromatic nitriles were recovered by distillation with steam or by extraction with ether. The residue, or insoluble non-volatile portion, was then crystallised from alcohol or ether. We submit a few of our experiments in detail.

### 1. *Acetonitrile on Acetic Acid.*

This is a repetition of one of Gautier's experiments. We heated 8.2 grams of acetonitrile and 12 grams of acetic acid in a sealed tube at 250° for seven hours. On opening the tube no pressure was noticed. Instead of distilling the contents of the tube, as Gautier did, we found it better to evaporate to dryness in a dish on the water-bath. A solid residue remained. This dissolved in ether, and, left to itself, the solution deposited white crystals, which were recognised as the diacetamide (m. p. 82°) described by Strecker<sup>1</sup> and Gautier. The reaction may be written thus:



### 2. *Acetonitrile on Benzoic Acid.*

Five tubes were filled each with a mixture of 4 grams of acetonitrile and 12 grams of benzoic acid. They were all heated at 150°–160° for three hours. One tube was then opened and the solid crystalline contents furnished nearly the original quantity of benzoic acid. The four remaining tubes were further heated as follows: After five hours at 175° and five hours at 200° they appeared to be unchanged, but after heating five hours longer at 220° the contents of the tubes had changed color and apparently consisted of white crystals wet with a brown liquid. A second tube was then opened. The crystals all dissolved in dilute sodium carbonate and proved to be unaltered benzoic acid. Acetic acid was also recognised here. The brown liquid was extracted with

<sup>1</sup>Ann. Chem. (Liebig) **103**, 327.

ether, which on evaporation left a residue of benzonitrile to the extent of 3 grams. The three remaining tubes were now heated for six hours at 220°–230°, for seven hours at 230°–240°, and for eight hours at 250°–260°. The contents had by this time become completely liquid. A third tube was then opened, and from it we obtained a smaller quantity of benzoic acid, a larger quantity of acetic acid, and 7 grams of benzonitrile. From a fourth tube opened about this time we obtained, by cautious evaporation of the benzonitrile extracted from it, a very small quantity of acetobenzamide,  $C_6H_5.CO.NH.CO.CH_3$ , which will be described later. The fifth and last tube was further heated for seven hours at 280°. The contents, extracted in the same way, gave the same quantities of the same products as the third tube. The reaction has therefore been different from what we expected. The two alcohol residues have exchanged their carboxyl and cyanogen groups, thus:



and at a temperature of 260° the yield of benzonitrile has amounted to 70 per cent. of the theoretical quantity. The production of acetobenzamide in the fourth tube is explained by supposing that the benzonitrile and acetic acid first formed react further upon each other, thus:



### 3. Acetonitrile on Phenyl-acetic Acid.

4 grams of acetonitrile and 13.6 grams of phenyl-acetic acid were heated for twenty hours at 250°. The tube was rinsed out with weak sodium carbonate solution and the residue dissolved in ether. The ether on evaporation furnished a small quantity of benzyl cyanide, besides a crystalline residue. This latter was washed with cold alcohol and recrystallised from hot alcohol. We thus obtained long white needles, melting at 192°. An elementary analysis furnished results which agree with the composition of diphenyl-diacetamide  $\begin{matrix} C_6H_5.CH_2.CO \\ C_6H_5.CH_2.CO \end{matrix} > NH$ .

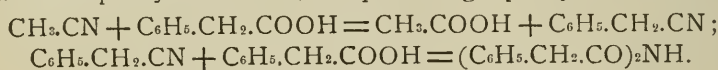
I. 0.2010 gram substance gave 0.1111 gram  $H_2O$  and 0.5587 gram  $CO_2$ .

II. 0.2263 gram substance gave 11.5 cc. nitrogen, measured at 26° and 766 mm.



	Found.		Calculated for $C_{16}H_{15}NO_2$ .
	I.	II.	
C	75.80	...	75.87
H	6.14	...	5.96
N	...	5.68	5.53
O	...	...	12.64

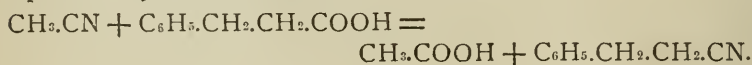
The composition of this body was further proved by saponifying it with sodium hydrate, when it gave only phenyl-acetic acid and ammonia. In the alkaline water used for rinsing the tube we recognised acetic and phenyl-acetic acids. Therefore in this experiment the cyanogen and carboxyl groups have in part exchanged places and the resulting benzyl cyanide has combined with some of the unaltered phenyl-acetic acid, thus producing diphenyl-diacetamide:



#### 4. Acetonitrile on Phenyl-propionic Acid.

4 grams of nitrile and 15 grams of acid were heated for twenty hours at  $250^\circ$ . The product of the reaction was a dark brown oil. This was agitated with soda solution to remove unaltered phenyl-propionic acid, and then distilled with steam. A nearly colorless oil passed over, which was recognised by its odor and by its boiling point ( $255^\circ$ ) as phenyl-propionitrile. It was completely saponified by sodium hydrate, yielding 2 grams of phenyl-propionic acid.

The conversion of phenyl-propionic acid into the corresponding nitrile under the influence of acetonitrile was therefore in this case only partial. But in another trial, where we used 8 grams of acetonitrile and 15 grams of phenyl-propionic acid, we obtained a yield of nearly 13 grams of phenyl-propionitrile. We have in fact used this method to prepare a considerable quantity of phenyl-propionitrile for further experiments. None of our experiments under this head have yielded a secondary amide. The following equation expresses the reaction:



#### 5. Propionitrile on Acetic Acid.

Equal molecules of these substances, with three drops of acetic anhydride, were heated in a sealed tube for seven hours at  $250^\circ$ .



The contents of the tube were then evaporated to dryness in a dish on a water-bath. A solid residue remained which was crystallised from ether. We thus obtained white needles which had a melting point of 86°.

This is really a repetition of another of Gautier's experiments. By the reaction of the same materials he obtained a compound which he called diacetopropiondiamide (m. p. 68°). Our crystals (m. p. 86°), which were isolated by a method different from his, furnished on analysis the following results :

I. 0.0463 gram substance gave 0.03305 gram H<sub>2</sub>O and 0.0885 gram CO<sub>2</sub>.

II. 0.1018 gram substance gave 11.6 cc. nitrogen, measured at 26° and 761 mm.

	I.	Found.	II.	Calculated for Diacetopropiondiamide, (CH <sub>3</sub> CO) <sub>2</sub> NH + CH <sub>3</sub> CH <sub>2</sub> .CO.NH <sub>2</sub> .	Calculated for Acetopropionamide, CH <sub>3</sub> CH <sub>2</sub> CO>NH. CH <sub>3</sub> CO>NH.
C	52.13	...	...	48.28	52.17
H	7.93	...	...	8.05	7.83
N	...	12.29	...	16.09	12.17
O	...	...	...	27.58	27.83

Our compound therefore corresponds in composition more nearly to acetopropionamide than to Gautier's product. The small yield which we obtained has precluded any further experiments upon it. The reaction may be written thus :



## 6. Propionitrile on Propionic Acid.

11 grams of nitrile and 15 grams of acid, with three drops of acetic anhydride, were heated at 250° for seven hours. The product of the reaction was a dark-colored liquid containing long needle-like crystals. The whole contents of the tube were evaporated to dryness on a water-bath and the solid residue crystallised from ether. Long white needles were formed, melting at 152°, which are probably the dipropionamide. Analysis and investigation of this substance were discontinued in consequence of the appearance of an article by Otto and Tröger<sup>1</sup> describing the formation and properties of dipropionamide.

<sup>1</sup> Ber. d. chem. Ges. 23, 759.

7. *Benzonitrile on Acetic Acid.*

30 grams of nitrile, eighteen grams of acid and three drops of acetic anhydride were heated in a sealed tube at  $220^{\circ}$  for five hours. The contents of the tube were evaporated to dryness on a water-bath and the residue crystallised from alcohol. White crystals were obtained which had a melting point of  $115^{\circ}$ . The yield was significant. Analysis of these crystals furnished the following figures:

I. 0.2145 gram substance gave 0.1116 gram  $H_2O$  and 0.5201 gram  $CO_2$ .

II. 0.2009 gram substance gave 0.1033 gram  $H_2O$  and 0.4878 gram  $CO_2$ .

III. 0.2050 gram substance gave 16 cc. nitrogen, measured at  $20^{\circ}$  and 760 mm.

	I.	Found. II.	III.	Calculated for $C_6H_5.CO > NH.$ $CH_3.CO > NH.$
C	66.13	66.22	...	66.26
H	5.78	5.71	...	5.52
N	...	...	8.71	8.59
O	...	...	...	19.63

Heated with alcoholic potassium hydrate, the substance yields ammonia, acetic acid and benzoic acid, and we think, therefore, that it is acetobenzamide,  $C_6H_5.CO.NH.CO.CH_3$ . It is readily soluble in hot water, in alcohol and in benzene. Addition of sodium to the solution in benzene causes evolution of hydrogen and precipitation of the sodium compound. We have prepared the silver compound also.

The reaction which has produced acetobenzamide is probably  $C_6H_5.CN + CH_3.COOH = C_6H_5.CO.NH.CO.CH_3$ . (Compare Exp. 2.)

8. *Benzonitrile on Phenyl-acetic Acid.*

10 grams of nitrile and 13.6 grams of acid, with three drops of acetic anhydride, were heated for five hours at  $200^{\circ}$ , then for five hours at  $240^{\circ}$ , and finally for two hours at  $260^{\circ}$ . We obtained here a solid product which was at once crystallised from hot alcohol. White crystals were isolated having a melting point of  $171^{\circ}$ . The yield was good. Analysis shows that they are probably phenyl-acetobenzamide.

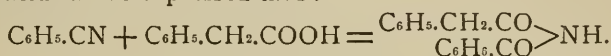
I. 0.2000 gram substance gave 0.1043 gram  $H_2O$  and 0.5521 gram  $CO_2$ .

II. 0.1985 gram substance gave 10.2 cc. nitrogen, measured at 26° and 775 mm.

	I.	Found.	II.	Calculated for $\begin{smallmatrix} \text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO} \\ \text{C}_6\text{H}_5\cdot\text{CO} \end{smallmatrix} > \text{NH}.$
C	75.28	...	...	75.31
H	5.79	...	...	5.44
N	...	5.82	...	5.85
O	...	...	...	13.39

Treated with two molecules of sodium hydrate in alcoholic solution the substance gave ammonia and a mixture of benzoic acid and phenyl-acetic acid.

It is evident that the reaction between benzonitrile and phenyl-acetic acid can be expressed thus :



#### 9. Benzonitrile on Phenyl-propionic Acid.

5 grams of nitrile and 7 grams of acid, with five drops of acetic anhydride, were heated for five hours at 200°, five hours at 240°, and two hours further at 260°. The product, purified in the usual way, furnished a good yield of transparent white needles when crystallised from alcohol. They melted at 106°. On saponification with sodium hydrate they gave off ammonia and yielded benzoic acid and phenyl-propionic acid. The ultimate analysis gave results agreeing with the composition of phenyl-propionbenzamide,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ .

	I.	Found.	II.	Calculated for $\text{C}_{16}\text{H}_{15}\text{NO}_2$ .
C	75.71	...	...	75.89
H	6.06	...	...	5.93
N	...	6.06	...	5.53
O	...	...	...	12.65

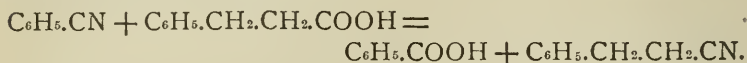
The following reaction, therefore, has taken place :



Another tube was filled with double the above quantities of nitrile and acid and heated for twenty hours at 280°. The product was purified as usual and furnished a very small amount of the phenyl-propionbenzamide ; but 7 grams of benzoic acid were obtained from the alkaline wash-water, and nearly 10 grams of

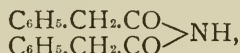
phenyl-propionitrile,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$ , boiling from  $253^\circ$  to  $256^\circ$ , were furnished by the ether extraction. The fact that phenyl-propionitrile was formed was further proved by converting it into phenyl-propionic acid by saponification with sodium hydrate.

The longer-continued heating at a higher temperature has in this case produced a different result from that obtained in the case of the first tube. The cyanogen and carboxyl groups have exchanged places, thus:



#### 10. *Phenyl-acetonitrile (Benzyl Cyanide) on Acetic Acid.*

Equal molecules of these materials were heated at  $260^\circ$  for six hours. We obtained in this case a mass of white crystals, which were washed with cold alcohol, to remove unaltered nitrile and acid, and then crystallised from hot alcohol. The purified substance formed white needle crystals melting at  $192^\circ$ . It corresponds in appearance and properties to the diphenyl-diacetamide,



described in Exp. 3. A nitrogen determination gave a result agreeing with the results of analysis of that substance. The yield was small. We account for the formation of diphenyl-diacetamide in this experiment by supposing that a part of the phenyl-acetonitrile became converted into phenyl-acetic acid, and that this then combined with the remaining phenyl-acetonitrile to form a simple secondary amide. If this were so we ought to find acetonitrile and phenyl-acetic acid as by-products, but we were unable to detect either of them.

#### 11. *Phenyl-acetonitrile on Benzoic Acid.*

Equal molecules of nitrile and acid were heated for five hours at  $240^\circ$ , and then two hours at  $260^\circ$ . The product, isolated as in the preceding experiment, formed, when crystallised from alcohol, long white needles whose melting point was  $171^\circ$ . The yield was good and no benzonitrile was found as by-product. The acids obtained on saponification and the figures furnished by elementary analysis lead us to the conclusion that this is the same phenyl-acetobenzamide produced in Exp. 8.

	Found.	Calculated for $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO} > \text{NH}.$ $\text{C}_6\text{H}_5\cdot\text{CO}$
C	74.91	75.31
H	5.86	5.44
N	5.35	5.85
O	...	13.39

The reaction is therefore parallel with that in Exp. 8,



### 12. Phenyl-acetonitrile on Phenyl-acetic Acid.

16 grams of nitrile and 19 grams of acid were heated at 250° for ten hours. After washing out the excess of phenyl-acetic acid by dilute soda solution and rinsing the residue with cold alcohol to remove any unaltered phenyl-acetonitrile, there remained a crystalline mass which, dissolved in hot alcohol and left to cool, deposited the same white needle crystals of diphenyl-diacetamide (m. p. 192°) obtained in Exps. 3 and 10. The yield was unusually good. The following figures were obtained on analysis:

I. 0.2005 gram substance gave 0.1076 gram  $\text{H}_2\text{O}$  and 0.5544 gram  $\text{CO}_2$ .

II. 0.2059 gram substance gave 10.4 cc. nitrogen, measured at 22° and 767 mm.

	I.	Found.	II.	Calculated for $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO} > \text{NH}.$ $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}$
C	75.41		...	75.87
H	5.96		...	5.96
N	...		5.77	5.53
O	...		...	12.64

When saponified by alcoholic sodium hydrate the diphenyl-diacetamide yielded ammonia and the theoretical quantity of phenyl-acetic acid. It is therefore a secondary diacid amide. The reaction by which it is formed may be thus represented:



Diphenyl-diacetamide is soluble with difficulty in cold alcohol but dissolves readily in hot. It is slightly soluble in hot water.

We have tried other nitriles and acids than those mentioned and have made some fifty experiments altogether. We select twenty of them, including the twelve foregoing, and place our results in a tabular form.

MATERIALS.				PRODUCTS.			
NITRILE.	ACID.	TEMP.	HOURS.	NITRILE.		ACID.	SECONDARY AMIDE.
				NAME.	d. n. D.		
Acetonitrile.....	Acetic acid.....	250°	7	.....	.....	.....	Diacetamide..... (CH <sub>3</sub> CO) <sub>2</sub> NH.....
".....	Benzoic acid.....	260	4	Benzonitrile.....	192°	Acetic acid...	Aceto-benzamide..... C <sub>6</sub> H <sub>5</sub> .CO.NH.CO.CH <sub>3</sub> .....
".....	Phenyl-acetic acid...	250	20	Phenyl-acetonitrile	232	" "	Diphenyl-diacetamide..... (C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> CO) <sub>2</sub> NH.....
".....	Phenyl-propionic acid	250	20	Phenyl-propionitrile	255	" "	.....
Propionitrile.....	Acetic acid.....	250	7	.....	.....	.....	Aceto-propionamide..... CH <sub>3</sub> .CH <sub>2</sub> .CO.NH.CO.CH <sub>3</sub> ...
".....	Propionic acid.....	250	7	.....	.....	.....	Dipropionamide..... (CH <sub>3</sub> .CH <sub>2</sub> .CO) <sub>2</sub> NH.....
".....	Ortho-toluic acid.....	235	5	Ortho-toluic nitrile	204	Propionic acid	.....
".....	Meta-toluic acid.....	235	5	Meta-toluic nitrile.	212	" "	.....
".....	Cinnamic acid.....	235	5	Cinnamic nitrile...	257	" "	.....
Benzonitrile.....	Acetic acid.....	220	5	.....	.....	.....	Aceto-benzamide..... C <sub>6</sub> H <sub>5</sub> .CO.NH.CO.CH <sub>3</sub> .....
".....	Benzoic acid.....	260	4	.....	.....	.....	Dibenzamide..... (C <sub>6</sub> H <sub>5</sub> .CO) <sub>2</sub> NH.....
".....	Phenyl-acetic acid...	250	7	.....	.....	.....	Phenyl-acetobenzamide... C <sub>6</sub> H <sub>5</sub> .CO.NH.CO.CH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> ...
".....	Phenyl-propionic acid	250	7	.....	.....	.....	Phenyl-propionbenzamide.. C <sub>6</sub> H <sub>5</sub> .CO.NH.CO.C <sub>2</sub> H <sub>4</sub> .C <sub>6</sub> H <sub>5</sub> ...
".....	" "	280	20	Phenyl-propionitrile	255	Benzoic acid..	.....
Phenyl-acetonitrile.	Acetic acid.....	260	6	.....	.....	.....	Diphenyl-diacetamide..... (C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> .CO) <sub>2</sub> NH.....
".....	Propionic acid.....	230	12	.....	.....	.....	Phenyl-acetopropionamide C <sub>2</sub> H <sub>5</sub> .CO.NH.CO.CH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> ...
".....	Butyric acid.....	230	12	.....	.....	.....	Phenyl-acetobutyramide.. C <sub>2</sub> H <sub>7</sub> .CO.NH.CO.CH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> ...
".....	Benzoic acid.....	250	7	.....	.....	.....	Phenyl-acetobenzamide... C <sub>6</sub> H <sub>5</sub> .CO.NH.CO.CH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> ...
".....	Phenyl-acetic acid...	250	10	.....	.....	.....	Diphenyl-diacetamide..... (C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> .CO) <sub>2</sub> NH.....
".....	Phenyl-propionic acid	250	7	.....	.....	.....	Phenyl-aceto-phenyl-propionamide C <sub>6</sub> H <sub>5</sub> .C <sub>2</sub> H <sub>4</sub> .CO>NH.....
							onamide C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> .CO.....

NAME.	FORMULA.	d. n. D.
Diacetamide.....	(CH <sub>3</sub> CO) <sub>2</sub> NH.....	82°
Aceto-benzamide.....	C <sub>6</sub> H <sub>5</sub> CO.NH.CO.CH <sub>3</sub> .....	115
Diphenyl-diacetamide.....	(C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> CO) <sub>2</sub> NH.....	192
.....	.....	...
Aceto-propionamide.....	CH <sub>3</sub> .CH <sub>2</sub> .CO.NH.CO.CH <sub>3</sub> .....	86
Dipropionamide.....	(CH <sub>3</sub> .CH <sub>2</sub> .CO) <sub>2</sub> NH.....	152
.....	.....	...
.....	.....	...
.....	.....	...
Aceto-benzamide.....	C <sub>6</sub> H <sub>5</sub> CO.NH.CO.CH <sub>3</sub> .....	115
Dibenzamide.....	(C <sub>6</sub> H <sub>5</sub> .CO) <sub>2</sub> NH.....	148
Phenyl-acetobenzamide...	C <sub>6</sub> H <sub>5</sub> CO.NH.CO.CH <sub>2</sub> .C <sub>6</sub> H <sub>5</sub> ..	171
Phenyl-propionbenzamide..	C <sub>6</sub> H <sub>5</sub> CO.NH.CO.C <sub>2</sub> H <sub>4</sub> .C <sub>6</sub> H <sub>5</sub> ..	106
.....	.....	...
Diphenyl-diacetamide.....	(C <sub>6</sub> H <sub>5</sub> .CH <sub>2</sub> .CO) <sub>2</sub> NH.....	192
Phenyl-aceto-phenyl-propionamide	C <sub>6</sub> H <sub>5</sub> .C <sub>2</sub> H <sub>4</sub> .CO > NH.....	145



This table shows on the left hand the nitriles and acids selected, with the number of hours and the temperatures at which they were heated. The products which we have thus far isolated and identified—nitrile, acid or secondary amide—are given in the proper right-hand columns. In cases where an amide was formed, other columns show its formula and melting point. These amides are all soluble in hot alcohol and most of them crystallise on cooling. Saponification with the calculated quantity of sodium hydrate gave in each case ammonia and the appropriate acids. In every case where a nitrile was one of the products it was identified by its boiling point and also by converting it into the corresponding acid.

The experiments with propionitrile on ortho-toluic, meta-toluic and cinnamic acids, and with phenyl-acetonitrile on propionic, butyric and phenyl-propionic acids, need no special description.

The examples in this table were not selected with the idea of advancing any particular theory; they embrace all the experiments made with these four nitriles. In a future article we shall give the results obtained with other nitriles. The reactions here involved may be summarised into three groups:

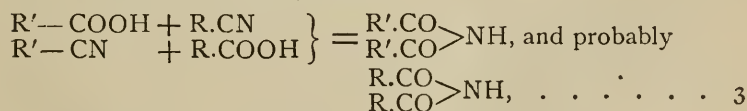
The nitrile and acid have condensed into a secondary, or diacid, amide, thus:



The alcohol radicles have exchanged their cyanogen and carboxyl groups:



In two instances the latter reaction was evidently accompanied by a tendency on the part of the products to condense with some of the unaltered materials, thus:



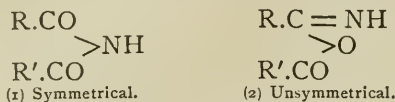
So far as these experiments indicate, we note that:

1. Fatty nitriles and fatty acids have given secondary amides.
2. Fatty nitriles and aromatic acids have exchanged their cyanogen and carboxyl groups, giving fatty acids and aromatic nitriles.
3. Aromatic nitriles and fatty acids have given mixed secondary amides.

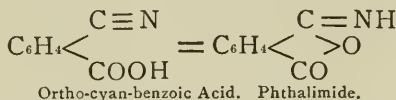


4. Aromatic nitriles and aromatic acids have given secondary amides, with the exception of one instance where the temperature was unusually high. In that case the product was a nitrile of the higher radicle.

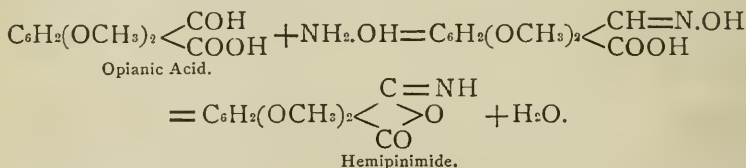
There are two possible constitutional formulæ for these secondary amides:



The first is the one generally accepted. An argument in favor of the second formula is, that ortho-cyan-benzoic acid, obtained from ortho-amido-benzoic acid by Sandmeyer's<sup>1</sup> reaction, on standing changes into phthalimide. This change is entirely analogous to the reaction which has produced the above-described secondary amides, and Liebermann<sup>2</sup> explains it thus:



Several reasons exist for considering this formula to represent the structure of phthalimide. Liebermann gives one reason by showing that opianic acid reacts with hydroxylamine, the final product being hemipinimide:



This reaction seems to be more easily explained by the unsymmetrical formula.

Further experiments will be necessary to determine which constitutional formula is to be assigned to the secondary amides described in this paper.

ORGANIC LABORATORY, SCHOOL OF MINES, COLUMBIA COLLEGE, NEW YORK CITY.

<sup>1</sup> Ber. d. chem. Ges. **18**, 1496.

<sup>2</sup> Ibid. **19**, 2281.

Contributions from the Chemical Laboratory of the Department of Agriculture.

## XVI.—ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.

BY W. MAXWELL.

These investigations have been conducted with the purpose of acquiring some further data showing the comparative proportions of matters which become separated from vegetable organisms under treatment with pure ether in varying durations of time. It has likewise been attempted to determine whether the whole of the substituted glycerides, or lecithines, may be separated by direct extraction with ether alone.

The following experiments were made with the seeds of *Gossypium* (cotton seed), the materials being reduced to the greatest state of fineness and the extractions made with the "Knorr" extraction apparatus. The calculations are reduced to the standard of water-free material.

The preliminary analyses which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time, gave the following results :

Time.	Weight of material. Grams.	Weight of extract. Grams.	Mean of 4 analyses. Per cent.
8½ hours,	4.0	1.472	37.39
10    "	4.0	1.491	37.87
15    "	4.0	1.511	38.38

These results, although based upon the mean of four analyses, were accepted only as following a number of tests previously made as preparatory observations.

It will be observed that an increased quantity of substance is separated with an extension of the period of extraction. The proportion of the increase is, however, small; and it is not conclusive as showing that the greater duration of time causes an increase in the fatty bodies only, as other constituents of vegetable organisms can be affected by a very protracted treatment with ether. In consequence of these reasons it has been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether during a period of 15 hours.

In considering this estimation of the proportions of glycerides and substituted glycerides or lecithines which are contained in the ether extract, the presence of other bodies, which have been removed by the ether, makes it impossible, in the absence of an absolute analysis of the extract, to determine accurately the quantitative relations of those fatty bodies. The ether extracts of plant matters contain in most instances varying amounts of the cholesterins, and, in some instances, of solid hydrocarbons, and these bodies may constitute several per cent. of the extract, as has been shown by E. Schulze<sup>1</sup> and others. Although the precise percentage of the normal glycerides cannot be estimated without an absolute analysis of the total ether extract, the substituted glycerides, or lecithines, may be determined with absolute accuracy, as the estimation of these bodies is based upon the proportion of phosphorus contained in the ether extract. The extract is burned with mixed alkali salts, by which process the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate. The phosphorus is determined in the usual way as magnesium pyrophosphate, and the weight of the latter body, multiplied by the accepted Hoppe-Seyler factor, gives the amount of lecithine.

7.27

A further series of extractions of the finely powdered cotton seed material was made with pure ether for a period of 15 hours each and the total extract determined. The proportion of lecithines contained in the extract was determined by the method already given, the residue of the extract being considered as composed of glycerides and other bodies. The means given by eight analyses were as follows:

Material. Grams.	Extract. Grams.	Mg. pyrophosphate. Grams.	L. in extract. Per cent.	L. in seed. Per cent.
4.0	1.513	0.00225	1.08	0.409

It will be shown by the following investigations that the proportion of substituted glycerides, or lecithines, stated (0.409 per cent.) does not represent the total lecithines present in the cotton seed.

The observation was made simultaneously by Prof. E. Schulze at Zürich and myself at Harvard College, that the lecithines are not wholly separated by treatment of the vegetable material with ether even for a long period of time. Prof. Schulze<sup>2</sup> observed

<sup>1</sup> Ztschr. physiol. Chem. 14, 491.

<sup>2</sup> Ibid. 13, 365.

that the results obtained by me in determinations of the amounts of lecithines contained in given seeds were too low, as the following numbers indicate :

	<i>Vicia sativa.</i>	<i>Faba vulgaris.</i>
W. Maxwell	= 0.55 per cent.	0.60 per cent.
E. Schulze	= 1.22	0.81

At the same time that Prof. Schulze was making the above observations with the seeds of the vetch and horse-bean, I, in experiments made with *Phaseolus vulgaris*, arrived at the same conclusion, viz., that the lecithines are not capable of a complete separation when the material is treated with ether alone. It was found that if the material which had been treated with ether were further extracted with absolute alcohol, a second portion of lecithines was obtained, which, in most instances, was greater than the proportion separated by the ether. The material, which had already been extracted for 15 hours with ether, was extracted for 6 hours with absolute alcohol. The alcoholic extract was evaporated to dryness, and the residue immediately re-extracted with ether. The reason for taking up the lecithines out of the alcohol extraction residue was, in the first place, on account of the observation that those lecithines which were originally insoluble in ether are capable of being dissolved by ether after they have been separated from the vegetable material by the treatment with alcohol; and further, the re-extraction with ether was made in order to avoid any possible small portion of inorganic phosphates which might have been removed from the plant material by the treatment with alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol. The following numbers indicate the proportions of fatty bodies separated by extraction with ether alone, and with ether, followed by the alcohol-ether, as described already, and the amounts of lecithines contained in the respective extracts :

Solvent.	Material. Grams.	Extract. Grams.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Grams.	L. in extract. Per cent.	L. in seed. Per cent.
Ether	4.0	1.513	0.00225	1.08	0.409
Ether + alcohol-ether	4.0	1.603	0.00516	2.306	0.94

The results given, as obtained by the successive treatment with ether and alcohol-ether, are the means of eight analyses.

The experiments have shown that not only are the lecithines not wholly separated by treatment with ether, but that even the

greater portion of these bodies resists the action of the ether, and may be separated only by the succeeding treatment with alcohol-ether. In the example of the cotton seed, the proportion of lecithines in the total fatty bodies is very small, yet it has been shown that more than 50 per cent. of the substituted glycerides are left in the material after extraction with ether for a period of 15 hours. If certain other varieties of seeds be considered, such as the legumes quoted in a previous place, it has been found that the total ether and alcohol-ether extracts of those seeds—which seeds contain from 2.5 per cent. to 4 per cent. respectively of fatty bodies—are composed of proportions of lecithines varying from 25–45 per cent. If, as has been shown, as much as 50 per cent. of the lecithines may remain unseparated after treatment of the materials with ether only, it is thus apparent that, in the examples of seeds in which the fatty bodies are composed of the large proportions of lecithines stated, from 20–25 per cent. of these fatty bodies remain undetermined in all estimations where ether only is used.

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## XVII.—ON THE BEHAVIOR OF THE FATTY BODIES, AND THE ROLE OF THE LECITHINES, DURING NORMAL GERMINATION.

BY W. MAXWELL.

In a preceding article, treating of “Methods of Estimation of the Fatty Bodies in Vegetable Organisms,” the author has shown the dissimilar behavior of the glycerides and lecithines under the action of given solvents. It has been observed that when certain vegetable materials are treated with pure ether for a given period of time, the normal glycerides are wholly dissolved; but, on the other hand, only a part, and in some instances less than 50 per cent., of the lecithines are directly acted upon by the ether; and further, that only under the action of absolute alcohol can the residue of these substituted glycerides, which are left in the material after extraction with ether, be entirely separated.

The study of the respective glycerides under the action of artificial solvents, though suggestive of, was preliminary to, the investigation of these bodies, and of the lecithines especially, under the influences of normal germination.



The presence of bodies in vegetable organisms, such as the cholesterins, hydrocarbons, etc., which may be separated from the material with the fatty bodies by treatment with ether and alcohol, makes it impracticable to attain definite results in respect of the normal glycerides without an absolute analysis of the total extract, *i. e.*, without saponifying the extracts and determining severally the saponification products. Moreover, the germinated materials yield still greater quantities of non-fatty bodies to the action of ether and alcohol, and the difficulty of the estimation of the normal glycerides in the mature seed thus becomes aggravated in the germinated materials. The pursuit of the lecithines in the products of germination may be made on the same principle as is the estimation of these bodies in the mature seed, which rests upon the determination of the organic phosphorus separated from the materials with ether and alcohol-ether as magnesium pyrophosphate and the calculation of the lecithines from that compound by means of the Hoppe-Seyler factor. 7.27

The following investigations will indicate the disposition of the fatty bodies in general under the action of germination. The specific purpose, however, has been the observation of the lecithines during the initial stages of growth, and under the influences of the ferments of the vegetable organism.

The preparation of the germinated seed-materials was as follows: The seeds of *Phaseolus vulgaris* were prepared in the propagating house of the Botanical Garden connected with Harvard College, and under the direction of Professor Goodale. The other varieties were germinated in the propagating house of the Department of Agriculture, Washington. The seeds were planted under the conditions of light, temperature and moisture as approximately normal as those of a propagating house can be made. The growth was stopped in the several stages at specific terms of development, and not at the end of specified periods of time, as is usual. The checking of the growth was done by placing the materials in an oven at a temperature of 90° C. The stages of growth at which the germination was stopped were marked by the following indications of development:

*1st Stage.*—The radicle had protruded through the testa about three-fourths of an inch. After drying, the seed and radicle together were ground to a fine powder.

*2d Stage.*—The plumule was developed and the radicle proportionally increased.

3d Stage.—The reserve materials of the mother-seed had become wholly used up, nothing but the testa remaining. So that in the last stage the plantlet itself formed the material, and at that period of its development when dependence on the outer world was attained.

The study of the seeds of *Phaseolus vulgaris* was conducted in the laboratory of Harvard College in 1889. The results obtained with this variety will be given in detail and first in order. The work upon the other varieties, cotton seed and maize, was done later in the laboratory of the Department of Agriculture.

*Phaseolus vulgaris* (mature seed).

Material.	Extract.	Per cent.
(1). 5.006 grams:	0.161 gram.	3.216
(2). 5.872	0.184	3.133
Mean = 3.174		

The proportion of lecithines contained in 100 parts of the extract and 100 parts of the material was found to be as follows :

Material. Grams.	Extract. Grams.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Grams.	L. in material. Per cent.	L. in extract. Per cent.
10.877	0.345	0.01397	0.933 .0351	29.394

No. 1 Stage Germination.

Material.	Extract.	Per cent.
(1). 10.13 grams.	0.2725 gram.	2.69
(2). 6.827	0.1960	2.871
Mean = 2.78		

The percentages of lecithines in the extract and in material were as follows :

Material. Grams.	Extract. Grams.	Mg. phosphate. Grams.	L. in material. Per cent.	L. in extract. Per cent.
(1). 10.13	0.2725	0.0235	1.934	61.945
(2). 6.827	0.1960	0.0165	1.748	60.91
Means = 1.841			61.427	

No. 2 Stage Germination.

In this stage the mother-seed was wholly exhausted and the material of the experiment was composed of the young plantlet. The plantlet was divided into two sections by cutting its axis midway between the extremities, giving thus the radicle and the



plumule sections. The purpose of this division of the plantlet into radicle and plumule sections was in order to study these parts separately, and thus to be able to observe the distribution of the lecithines, if these bodies were present, in the general organism of the plantlet.

(a). Radicle section :

Material.	Extract.	Per cent.
(1). 5.5 grams.	0.2215 gram.	4.03
(2). 4.922	0.1865	3.79
Mean = 3.909		

The percentages of lecithines in the extract and in the material :

Material. Grams.	Extract. Gram.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Gram.	L. in material. Per cent.	L. in extract. Per cent.
(1). 5.5	0.2215	0.03	3.96	98.41
(2). 4.922	0.1865	0.025	3.48	91.90
Means =			3.72	95.15

(b). Plumule section :

Material.	Extract.	Per cent.
(1). 9.633 grams.	0.293 gram.	3.042
(2). 8.929	0.258	2.880
Mean = 2.961		

The percentages of lecithines in the extract and in the material :

Material. Grams.	Extract. Gram.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Gram.	L. in material. Per cent.	L. in extract. Per cent.
(1). 9.633	0.293	0.038	2.86	94.26
(2). 8.929	0.258	0.0315	2.63	88.00
Means =			2.75	91.13

Mean of radicle and plumule = 3.23 per cent.

The investigation of the two stages of germinated materials shows that the first-stage material contained twice the proportion, and the second stage three times the proportion, of lecithines which was found in the original or mature seed. The study of the two sections of the plantlet in the second stage indicates that the lecithines were equally distributed through the whole organism. The conclusions indicated by these results will be considered later.

### *Gossypium* (Cotton seed).

The results given in each number of the following series represent the mean of four determinations :

Material.				Extract.	Per cent.
Mature seed,	I	gram.		0.4076 gram.	40.764
No. 1 stage germ.	I	"		0.3022 "	30.220
" 2 "	"	I	"	0.1797 "	17.970
" 3 "	"	I	"	0.1082 "	10.820

Percentages of lecithines in the material and in the extract:¹

Material.				Extract. Gram.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Gram.	L. in material. Per cent.	L. in extract. Per cent.
Mature seed,	I	gram,		0.4076	0.001293	0.94	2.306
No. 1 stage,	I	"		0.3022	0.00296	2.15	7.110
" 2 "	"	I	"	0.1797	0.00274	2.00	11.080
" 3 "	"	I	"	0.1082	0.00180	1.308	12.00

It is shown that the first-stage germination material contained nearly three times the proportion of lecithines which was present in the mature seed; but the second, and, still more, the third stages indicated that the high proportion of those bodies which appears in the first stage had become in part reduced.

#### *Zea mays* (Maize).

In the work done with the maize variety large amounts of material were taken, it having been observed in the preliminary experiments that the proportion of lecithines contained in the corn is very small.

Material.				Extract.	Per cent.
Mature seed,	16	grams.		0.9122 grams.	5.70
No. 1 stage,	18	"		0.9169 "	5.09
" 2 "	18	"		1.0634 "	5.90
" 3 "	14	"		1.0374 "	7.41

Percentages of lecithines in the material and in the extract:

Material.				Extract. Gram.	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . Gram.	L. in material. Per cent.	L. in extract. Per cent.
Mature seed,	16	grams.		0.9122	0.0041	0.186	3.300
No. 1 stage,	18	"		0.9169	0.0048	0.193	3.800
" 2 "	18	"		1.0634	0.0079	0.319	5.400
" 3 "	14	"		1.0374	0.0084	0.436	5.886

A comparison of the proportions of lecithines contained in the mature seeds, and in the materials of the several stages of germination of the three varieties of seeds under investigation, is shown as follows:

¹ The analytical work in these examples was made by Mr. Omar Carr.

	<i>Phaseolus vulgaris.</i>	<i>Gossypium.</i>	<i>Zea mays.</i>
Mature seed,	0.933 per cent.	0.94 per cent.	0.186 per cent.
No. 1 stage,	1.841	2.15	0.193
" 2 "	3.230	2.00	0.319
" 3 "	...	1.308	0.436

The estimation of the proportions of the lecithines contained in the germination materials of the varieties of seeds specified has been based on the principle that the organic phosphorus found in the ether and alcohol-ether extracts of these materials is present in the form of lecithine. It is not, however, conclusive that the phosphorus separated by the given solvents was in combination with a glyceride. In order to have a proof that the phosphorus compound separated from the material of the germinated seeds was a lecithine, it was necessary to examine the decomposition-products of the latter body, which was supposed to be contained in the extracts of the materials. For this purpose was taken the No. 3 stage germination-material of the cotton seed, in which the mature seed had been wholly used up and the material consisted wholly of the young plantlet. About 30 grams of this material were extracted, and, after evaporating off the ether and alcohol, the extract-residue was boiled for about half an hour with barium hydroxide. After removal of the excess of barium and partial evaporation of the solution, a very large quantity of barium stearate separated out in a well-crystallised form. After the separation of the barium stearate salts the solution was evaporated to a thick syrup, which was extracted with 99 per cent. alcohol containing 1.5 per cent. hydrochloric acid. If cholin, the most characteristic of the decomposition-products of a lecithine, were contained in the syrup-residue, it would be taken up by the alcohol and thus separated from the glycerin-phosphoric acid compound, the latter body being insoluble in alcohol. The alcohol-hydrochloric acid extract, after treatment with animal charcoal, was reduced to a great concentration and a solution of platinum chloride added, which gave a heavy, voluminous, yellow precipitate, soluble in water. The water solution of the platinum double-salt of the base was treated with hydrogen sulphide, the platinum sulphide removed, and the solution evaporated to a small volume. The aqueous solution of the hydrochloride of the base gave reactions with the given reagents which are strictly characteristic of cholin :

With phosphotungstic acid,	white precipitate.
" phosphomolybdic "	yellow "
" potassium-bismuth-iodide, red	"
" iodine-potassium-iodide, brown	"
" chloride of gold,	yellow " soluble in water.

The residue, from which the cholin had been separated, was examined in respect of the presence of phosphoric acid, and the latter was identified by the use of ammonium molybdate. It has thus been established that the organic phosphorus-compound which was separated from the No. 3 stage germinated material by extraction with ether and alcohol-ether was a lecithine, which has been observed by the identification of its decomposition products.

Before reviewing the analytical data which have been given in respect of the conclusions which are indicated, certain observations may be included bearing upon the dissimilar behavior of the glycerides and the lecithines under simple mechanical pressure. It has been found that when the cotton seed is submitted to pressure for obtaining the oil, the normal glycerides become separated, and that the same quantity of lecithines which is found in the mature seed is found in the material from which the glycerides have been expressed. The observation was made with the cotton seed meal, in the form of cattle-food cakes, and the following data were obtained :

Material.	Extract. Per cent.	Lecithine in material. Per cent.	Lecithine in extract. Per cent.
Mature seed,	40.764	0.94	2.306
Cotton seed meal,	13.45	1.06	7.92

The normal and the substituted glycerides have shown dissimilar behavior under the respective actions of artificial solvents, mechanical pressure and germination.

In recapitulating the data obtained in the study of the given stages of germination or development of the seeds under investigation, certain conclusions are clearly indicated. It is apparent that the lecithine bodies are formed in the young plantlet during the initial and later stages of development. To exemplify this observation more clearly, the relative amounts of lecithines in the mature seed, and in the last stage of germination, give conclusive testimony. In the example of *Phaseolus vulgaris*, 100 parts of the water-free mature seed are equal to about 75 parts of the water-free No. 2 stage germinated material. It has been seen that the

relations between the lecithine amounts in the mature and germinated seeds are as follows:

$$\begin{array}{ll} \text{Mature seed} & = 0.933 \text{ per cent.} \\ \text{No. 2 germinated} & = 3.230 \end{array}$$

But as 75 parts of germinated material are the product of 100 parts of mature seed, the 3.23 per cent. found in the former material is reduced to 2.42 per cent., which shows that during the initial stages of growth, under normal conditions of light, heat and moisture, the lecithine bodies had become increased from 0.933 per cent. to 2.42 per cent., or by 159.0 per cent. In the examples of the cotton seed and maize the same observations have obtained, which are specially emphasised in the instance of *Zea mays*. The analytical data attaching to the cotton seed indicate that the maximum of the lecithine contents of the organism was reached in the No. 1 stage of the germination, and that in the later stages the plantlet had reconsumed a portion of the lecithine store.

It is thus apparent that the plantlet, during the incipient period of growth, under the influence of light, is capable of utilising the inorganic phosphorus present in the mother-seed for the formation of new lecithine bodies; and further, that the plantlet, at a later stage, and when it is becoming independent of the mother-seed, decomposes and utilises those bodies in its continued development. It has been said that the plantlet is capable of utilising the inorganic phosphorus in the organisation of the lecithines. That is made very clear by the observation that the period of organisation is during the first stage of growth, and during the time that the plantlet is deriving its whole support from the mother-seed.

The observations which have been made are not conclusive, however, that the whole of the lecithine bodies found in the young plantlet are the products of reorganisation. That portion in the young plantlet which is in excess of the proportion contained in the mature seed is most clearly a reorganisation product. It is possible, on the other hand, and the observations made in the study of the earlier stages of the germination make it appear probable, that all that portion of the lecithine bodies contained in the mother-seed passes over into the organism of the young plantlet without decomposition or change and becomes directly available for its development. The latter question, as to whether the lecithines



resist the action of the ferments of the vegetable organisation during germination and pass over from the mother-seed into the plantlet undecomposed, will be the subject of further research, and in connection with the further question whether the lecithines present in animal organisms are organised by the animal organs or taken up direct from vegetable substances.

## XVIII.—PINE TREE HONEY-DEW AND PINE TREE HONEY.

WITH NOTES ON THE NATURE OF THE DEXTROGYRATE BODIES IN HONEY.

BY H. W. WILEY.

In March, 1890, I received from Mr. W. M. Evans, of Amherst, Va., a sample of pine tree honey-dew and of pine tree honey.

The honey-dew, according to the description sent by Mr. Evans, was collected drop by drop from the pine leaves. At the same time Mr. Evans sent me a sample of pine tree honey which he says was, without doubt, made by the bees from the pine leaves during the winter, since no other honey-producing plants were accessible to them. Having seen it stated in some of the foreign journals that honey made from pine forests gave a right-handed polarisation, I thought it would be of interest to examine the two samples sent by Mr. Evans to determine, if possible, their nature. The small quantity of the honey-dew which I had at my disposal made, of course, a thorough study impossible. So far as could be determined, however, it had the following characteristics :

It contained 54.41 per cent. of water and 45.59 per cent. of solid matters. Calculated as dextrose it contained 17.44 per cent. of reducing sugar. After inversion it contained 26.03 per cent. of reducing sugar, which would indicate a content of sucrose equivalent to 8.16 per cent. At  $31^{\circ}$  by direct polarisation it gave an angular deviation equivalent to  $36^{\circ}.56'$  of the cane sugar scale (Ventzke). If we assume that the reducing sugar present was pure invert sugar, then the levogyrate influence of 17.44 per cent. of invert sugar at  $31^{\circ}$  would be equal to  $-4^{\circ}.97'$  of the cane sugar scale. Adding this number to the direct polarisation, it is seen that this would have amounted to 41.53 divisions of the scale.

Deducting from this number the right-handed polarisation due to the sucrose present, viz., 8.16, we have 33.37 divisions of right-handed rotation due to bodies other than sucrose present in the dew. The sum of the rotations of the invert sugar, viz., 17.44 per cent., and the sucrose 8.16 per cent., is 25.60 per cent. of the total solid matter due to sucrose and invert sugar. Deducting this number from the total solids present, viz., 45.59, there is left 19.99 per cent. solid matter which has caused the right-handed deviation of 33.37 divisions. This substance, therefore, has a specific rotatory power fully one-half greater than sucrose. It is not, therefore, due to pinite, but to some body or mixture of bodies having a specific rotatory power of  $(\alpha)_D = 105$  (circa.)<sup>1</sup> Having thus found that the pine tree exudation itself is a right-handed body, I naturally expected to find the honey made therefrom also right-handed; in this expectation, however, I was disappointed. The direct polarisation of the honey, under normal conditions at  $31^\circ$ , was  $-13$  divisions of the cane sugar scale, and the total reducing sugar which it contained, calculated as dextrose, was 70.42. Not only, therefore, was this sample of pine tree honey left-handed, but it was also left-handed to a degree greater than that ordinarily exhibited by honeys. From this fact the inference is to be drawn either that in gathering the honey the bees exerted upon it an inverting effect which made it left-handed, or else Mr. Evans was mistaken in supposing that the bees had derived their stock of honey from the trees in question.

The peculiar climatic conditions of last winter presented, through the whole season, the mildness of spring, affording, perhaps, an exceptional opportunity for the development of the pine tree honey-dew, and I am sorry that my attention was not called to the matter in time to have secured much larger quantities of this interesting substance.

The probable existence in honey of a right-handed body not sucrose or dextrose was indicated by me in a paper published in the "*American Apiculturist*," Vol. 3, No. 12, 1885. In this paper it is shown that a varying amount of substance, which I supposed then to be pure dextrin, was found in honey, amounting in this case to as much as 4 per cent.

Amthor has found<sup>2</sup> that honey gathered from pine forests con-

<sup>1</sup> This rotation would indicate that the body might be arabinose  $[(\alpha)_D = 105]$ , but there was not a sufficient amount of it definitely to determine this point.

<sup>2</sup> Rep. anal. Chem. 1885, 163.



tains dextrin, as he supposed at that time, even in such quantities as to become dextro-rotatory.

Klinger claims that this phenomenon is not confined exclusively to honey of coniferous origin. At that time I was led to express, in the paper referred to, my doubt of the truth of Lenz's observation<sup>1</sup> that after fermentation honey yields no optically-active substance. This doubt of mine has been confirmed by subsequent investigations.

Raumer<sup>2</sup> calls attention to the fact that the statement of Sieben, that the addition of starch syrup to honey could with certainty be detected by the residue of right-handed dextrin, is held to be unreliable. According to Sieben, 25 grams of honey dissolved in 150 cc. of water and treated with 12 grams pressed yeast (starch-free) are completely fermented in two days. The residue, clarified with aluminium hydrate and filtered, is completely inactive optically and does not reduce Fehling's solution. Even when treated with hydrochloric acid, to convert any starch or dextrin into dextrose, no reduction takes place. Raumer asserts that Sieben's observations must have been made on abnormal honeys.

Amthor has also called attention to the fact that honeys treated according to the method of Sieben, described above, showed right-handed polarisation, and that this phenomenon was supposed to be due to the honey having been largely gathered from pine forests. Honeys of known purity were found to be uniformly right-handed after fermentation. In three samples the dextrogyratory power, after fermentation, was expressed by the following numbers respectively:  $2^{\circ}.83$ ,  $1^{\circ}.58$ ,  $2^{\circ}.70$ . In three more samples of doubtful origin the numbers obtained were:  $2^{\circ}.13$ ,  $2^{\circ}.53$ ,  $3^{\circ}.23$  respectively.

In the first three samples all possibility of adulteration is positively excluded. It was also established that the bees had not been fed with glucose. It is well known that feeding glucose or ordinary sugar causes foul brood. Only pure rock candy can be used for such purposes.

It was next deemed of interest to determine the nature of this dextrogyratory body. In order to purify the fermentation residue as completely as possible the method of Schmidt for obtaining the so-called gallisin was employed.<sup>3</sup>

<sup>1</sup> Chem. Ztg. 8, 613.

<sup>2</sup> Ztschr. angew. Chem. 1889, 607.

<sup>3</sup> Ber. d. chem. Ges. 13, 1000.

The honey in 10 per cent. solution, after fermentation, was filtered and evaporated to a thin syrup and poured into absolute alcohol. The brownish precipitate thus obtained was rubbed with absolute alcohol, the liquid poured off, and the residue rubbed twice with 96 per cent. alcohol, separated on a filter, and treated three times with ether. The residue was next dissolved in a small quantity of water, treated with bone-black and filtered. If the water-clear solution is now poured into absolute alcohol, a snow-white precipitate is formed. When the precipitate has subsided the alcohol is removed with a siphon and the residue treated again with a mixture of water-free ether and absolute alcohol. After 36 hours it was found that the precipitate had settled well to the bottom. The liquid was poured off and the residue poured into a large asbestos filter previously weighed. The washing was performed three times with absolute alcohol and three times with ether, and a stream of dried hydrogen conducted over the residue, which caused it to fall into a pulverulent mass. Finally, it was dried in hydrogen at 60°. At this temperature the mass fell together into a lump. The filter was further dried 48 hours over sulphuric acid and weighed in a closed tube. The specific rotatory power for four samples of the substance, prepared as above, from four different kinds of honey, was as follows:

From Nürnberg honey, . . . . .	68.06
“ “ “ . . . . .	59.30
From honey from head gardener, Seyfferth, . . .	58.30
From Nürnberg honey, . . . . .	52.60

The reducing power of the body for Fehling's solution was determined for the first and second samples, both before and after inversion.

No. 1.

Before inversion, 1 gram substance reduced .455 gram copper.  
After inversion, 1 gram substance reduced 1.200 gram copper.

No. 2.

Before inversion, 1 gram substance reduced .3048 gram copper.  
After inversion, 1 gram substance reduced .845 gram copper.

It is evident from the foregoing that no single substance composes the unfermentable residue of honey, and it is further evident that this substance is not largely composed of dextrin. It was further established that the substance, after inversion, was fully

fermentable. Judged by its specific rotatory power above, this substance resembles Schmidt's gallisin, but its reducing power is quite different. The researches show that the purity of a honey cannot be safely determined by the fermentation process as practiced heretofore.

In regard to this right-handed body in honey, Amthor and Stern<sup>1</sup> have made some interesting investigations.

44.9655 grams of a sample of undoubtedly genuine honey were dissolved in 300 cc. water and allowed to ferment with yeast. After filtering and reducing to 200 cc. the liquid was examined in a Laurent polariscope and gave  $+24^{\circ}.9$  in a 20 cm. tube. The dextrin was then converted into dextrose by heating 100 cc. with 10 cc. hydrochloric acid for three hours in a water-bath. After cooling and making up again to 100 cc., the polarisation gave  $9^{\circ}.21$ , equal to 2.249 per cent. dextrose. Allihn's gravimetric process gave 2.266 per cent. The formation of dextrose points to the honey having contained dextrin. The authors further confirmed this view by preparing phenylglucoson. A large quantity of honey was fermented in a weak solution; the filtrate yielded, on evaporation, a brown, thickish syrup, which was really an impure dextrin. After dissolving in a little water, phosphotungstic acid, containing some sulphuric acid, was added and the liquid filtered. The excess of reagent was removed by means of baryta water, and this in turn by the cautious addition of sulphuric acid. After concentrating, a little *liquor plumbi* was added, the liquid filtered, and the excess of lead removed by means of hydrogen sulphide. The filtrate was evaporated in the water-bath until it became a thin syrup, and 200 cc. of 90 per cent. alcohol were added, which was sufficiently diluted to keep the dextrin in solution. After filtering and evaporating, the dextrin was obtained as a brown syrup, which was purified with animal charcoal, until it was finally obtained as a yellowish, brittle, amorphous mass.

To obtain the related glucose, 5 grams of this dextrin were dissolved in 200 cc. of water mixed with 20 cc. of 20 per cent. sulphuric acid, and heated for three hours on the water-bath. The liquid was neutralised with barium carbonate, filtered and evaporated to a syrup, which was repeatedly exhausted with alcohol. After distilling off, a brownish syrup was obtained, which was purified by animal charcoal.

<sup>1</sup> Zeitschr. angew. Chem. 1889, p. 575.

It crystallises in granules, reduces Fehling's solution strongly, and the authors succeeded in forming phenylglucoson by warming 1 gram with 2 grams of phenylhydrazin, 3 grams of sodium acetate and 20 cc. of water. The crude product was recrystallised from alcohol and obtained in small yellow needles fusing at  $204^{\circ}$  C. This removes all doubt about the original substance being dextrin, the presence of which in honey may perhaps be explained by the supposition of the bees feeding, when they get a chance, on malt in breweries.

From a careful study of the above data it is shown that the honey-like exudation of the pine tree, without doubt, differs in a marked degree from that of the honeys of ordinary plants in being right-handed, from a polariscopic point of view, and containing bodies not sucrose nor invert sugar, with a specific rotatory power of about 105. It appears further that, according to the observations of some authors, honey made from the exudation of pines is naturally right-handed, though this observation is not confirmed by the single sample which I had at my disposal.

I should be glad hereafter to receive samples of honey of undoubted pine tree origin, for the purpose of making a further study in regard to its nature, and I hope to take advantage of the next mild winter to obtain more extensive samples from the localities affording those samples already examined.

Up to the present time it must be confessed that no genuine sample of honey collected in this country has shown a right-handed rotation. Honey possessing this property therefore greatly excites suspicion, and warrants an inquiry concerning its composition.

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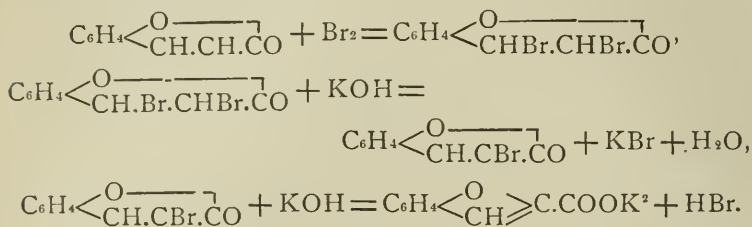
## ON COUMARONE.

BY A. R. L. DOHME.

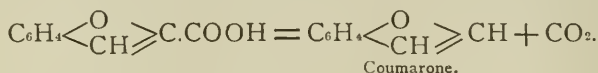
This substance was first made by Fittig and Ebert,<sup>1</sup> who obtained it by the distillation of coumarilic acid with lime, in the course of their work upon lactones and in particular upon the lactone coumarin. By treating this latter substance with bromine

<sup>1</sup> Ann. Chem. (Liebig) 216, 168.

and heating with alcoholic potash the dibrom addition-product thus formed, they obtained *a*-bromcoumarin, which, upon further treatment with caustic potash, yielded coumarilic acid, according to the following equations :



The transformation of coumarilic acid into coumarone, with loss of carbon dioxide, is represented by the following equation :



This represents Fittig's view of the constitution of coumarone, regarding it as a closed ring and as bearing the same relation to indol that furfuran bears to pyrrol. Rössing<sup>1</sup> also, somewhat later, obtained coumarone in the course of his work upon ortho-aldehydephenoxyacetic acid, from which he, however, first obtained coumarilic acid. Fittig found it to be a slightly yellow, highly refracting oil, possessing a characteristic aromatic odor, insoluble in water but quite easily volatile with water-vapor, completely insoluble in alkalis, and hence, in all probability, no phenol. Nascent hydrogen and fuming hydrobromic acid or hydriodic acid do not act upon it, while concentrated sulphuric acid causes it to change to a reddish-brown amorphous mass. Bromine, however, was found by these investigators to act quite readily upon the oil, yielding a dibrom addition-product which, upon treatment with boiling alcohol or alcoholic potash, yielded an oil volatile with water-vapor, and crystallising, upon cooling, to a mass of prisms which melt at 36° and are monobromcoumarone. Owing to lack of material they here left the subject, and no work was done upon it until Kraemer and Spilker,<sup>2</sup> during the past year, found that coumarone was a constant constituent of the light oils obtained in the distillation of coal-tar. Having thus found a ready means of obtaining coumarone in any desired quantity, they proceeded to make some experiments with it.

<sup>1</sup> Ber. d. chem. Ges. 17, 3000.

<sup>2</sup> Ibid. 23, 78.



repeating and verifying Fittig's work and trying the action of chlorine upon it. By the action of the latter reagent they obtained an oil boiling at  $245^{\circ}$ – $248^{\circ}$ , which is dichlorcoumarone, analogous to the dibrom addition-product obtained by Fittig. By treatment with alcoholic potash they also obtained the corresponding monochlorcoumarone, which melts at  $74^{\circ}$ – $75^{\circ}$  and boils at  $215^{\circ}$ – $217^{\circ}$ . The tarry product obtained by the action of concentrated sulphuric acid upon coumarone they name "paracoumarone," finding it to be a polymer of coumarone. Their synthesis of chrysene by heating together coumarone and naphthalene is also interesting, inasmuch as it shows that the oxygen atom of coumarone is removable without breaking down the entire molecule. Before the work of Kraemer and Spilker was published, the writer, at the suggestion of Prof. A. W. von Hofmann, undertook to experiment upon coumarone, hoping to get some well-crystallised derivatives, and from the reactions of these to throw some light upon the constitution of the substance. First, the action of aniline at all temperatures from  $190^{\circ}$  to  $280^{\circ}$  in sealed tubes was tried, but without any positive result, as most of the coumarone was changed to paracoumarone and the aniline remained unchanged. Concentrated ammonia was next tried, in the hope of replacing the oxygen atom by the imido-group and thus obtaining indol, but, even at  $280^{\circ}$  in sealed tubes, there was no sign of a reaction. The dibrom addition-product was made by treating the dry oil with bromine, when the former changes from an oil to a solid mass of white crystals. The melting point observed was  $88^{\circ}$ , which agrees with Fittig's and with Kraemer's figures. From this, monobromcoumarone was made by treating the dibromide with alcoholic potash. The mixture was distilled with steam, and the colorless oil that came over soon solidified to a mass of white crystals which melted at  $36^{\circ}$ , the melting point observed by Fittig. The action of aniline at  $200^{\circ}$  was tried upon this monobromcoumarone, in the hope of introducing the group  $C_6H_5NH$  in the place of the bromine atom. There was no reaction, however; even at  $280^{\circ}$  in sealed tubes no change could be observed in the contents of the tube, the monobromcoumarone separating out as such on adding water, while silver nitrate failed to show the presence of any trace of hydrobromic acid. Concentrated ammonia also did not act upon the monobromcoumarone when the two were heated together at  $280^{\circ}$ . The action of phosphorus pentachloride upon coumarone was

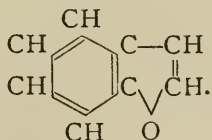
next tried, in the hope of thus replacing the oxygen atom, and from the resulting product drawing some conclusion as to the constitution of the substance. With this reaction in mind, molecular quantities of phosphorus pentachloride and coumarone were heated in sealed tubes at  $175^{\circ}$ , after it had been shown that no reaction took place when the constituents were heated even at  $200^{\circ}$  with an inverted condenser. The product of the reaction was a brown-colored oil, the reaction having generated a considerable quantity of hydrochloric acid, which, when the tube was opened, escaped under great pressure. The oil was fractionated and yielded three fractions, boiling respectively at  $70^{\circ}$ – $100^{\circ}$ ,  $210^{\circ}$ – $220^{\circ}$  and  $220^{\circ}$ – $250^{\circ}$ , there being, however, very little of the latter formed. After repeated fractionation, the first fraction was recognised as phosphorus trichloride, as it boiled at  $74^{\circ}$ – $76^{\circ}$ , while the second proved to be monochlorcoumarone, which had been obtained by Kraemer and Spilker, and which boiled at  $216^{\circ}$ – $218^{\circ}$ . The third fraction was, in all probability, some dichlorcoumarone, which, as found by the just mentioned authors, boils at  $245^{\circ}$ . In all probability, then, the phosphorus pentachloride has merely acted as a chlorinating agent and given up its two loosely-held chlorine atoms to the coumarone. Thus dichlorcoumarone was formed, which, at the high temperature prevailing, lost hydrochloric acid and formed monochlorcoumarone, the small portion of dichlorcoumarone found having probably not taken part in the latter reaction. Raising the temperature from  $175^{\circ}$  to  $280^{\circ}$  did not yield any products different from those obtained at  $175^{\circ}$ , so that it was clear that the oxygen atom of coumarone is certainly not loosely held in combination in the molecule. Next it was thought possible to remove this oxygen atom by heating the monochlorcoumarone just obtained with phosphorus pentachloride at a high temperature in a sealed tube, and thus obtain orthochlorotrichlorstyrene, or, if addition also took place, orthochlorotetrachlorethylbenzene. Five grams of the monochlorcoumarone were sealed in a tube with an excess of phosphorus pentachloride and heated at  $275^{\circ}$  for five hours. The product of the reaction was a brown-colored oil, which, upon distillation, yielded two products, one boiling at  $75^{\circ}$ , and hence being phosphorus trichloride, and the other boiling at  $255^{\circ}$ – $260^{\circ}$ . Hydrochloric acid was generated in quantity. The latter fraction, upon cooling, showed signs of crystallisation, and, being soluble in ether with great readiness, was set aside in a solution of the latter



reagent to crystallise. This it did in long, thin, white, satiny needles which melted at 57.5°–58°. Not very much of this, however, was obtained, and after two futile attempts to make a chlorine estimation according to Carius, the tubes exploding each time, the very small amount of the substance left was analysed and gave approximate figures for a dichlorocoumarone of the formula  $C_8H_4Cl_2O$ ,  $(C_6H_4 \begin{smallmatrix} O \\ \diagup \diagdown \\ CCl \end{smallmatrix} \geq CCl)$ .

o.1808 gram substance gave 0.2810 gram AgCl, which is equivalent to 38.4 per cent. chlorine, whereas the formula  $C_8H_4Cl_2O$  requires 37.96 per cent. chlorine. Owing to the close of the semester, no more of the substance could be made, and the verification of this substance will have to be postponed until a future investigation, when it is proposed also to study the action of phosphorus pentasulphide upon coumarone, inasmuch as a preliminary experiment showed that a reaction takes place between these substances. For when the oily product obtained by heating them together in a sealed tube at  $180^\circ$ , is distilled with steam, no coumarone could be detected in the receiver, thus showing that it must at least have been changed by the reaction, even if substitution had not taken place, for coumarone is very volatile with water-vapor.

The object in view in these experiments was to replace the oxygen atom of coumarone, and from the resulting compounds or reactions to deduce some argument for or against the Fittig-Hantzsch formula for the substance :



In so far as the experiments have any value whatever, being mostly negative, they tend to confirm rather than contradict this formula; for the stability of the coumarone molecule certainly was quite striking in the course of the work, and the difficulty experienced in attempting to replace the oxygenation also spoke in favor of the closed-ring formula for the substance. In conclusion, I would like to thank Prof. von Hofmann for his kindness to me and for the instruction I have received while working under his supervision.

## ON THE QUESTION OF CONCORDANCE IN ATOMIC WEIGHT DETERMINATIONS.

BY F. W. CLARKE.

In the determination of atomic weights the subject of constant errors has of late years received much attention. On the experimental side, that is with reference to individual series of data, the possibility of constant error is always carefully considered; but another phase of the question, involving antecedent values, is too apt to be ignored. Under the latter heading one special case is familiar to all chemists, namely, the uncertainty in the ratio between oxygen and hydrogen, in consequence of which we have two distinct standards for atomic weights, the one  $H = 1$ , the other  $O = 16$ . The difference between these standards is small in itself, but among the higher atomic weights it becomes multiplied to serious proportions. In other words, if the atomic weight of hydrogen be taken as unity, the uncertainty in the atomic weight of oxygen becomes a large constant error in the calculation of other values. This particular error is merely a type of its class; for whenever an atomic weight is computed from other atomic weights which are assumed to be known, their errors, together with the experimental errors of the determinations themselves, are accumulated in the final result. Thus it sometimes happens, when an atomic weight has been determined by different methods, involving the use of different compounds, that the concordance or discordance between the several series of data obtained may depend upon the factors assumed in the final calculation. These factors are themselves subject to errors, great or small, which become constant errors in calculation, and which, although cumulative in their effects, are commonly neglected altogether. Only those determinations of atomic weight which depend upon direct comparison of an element with the standard of value are free from errors of this class.

In a recent paper upon the atomic weight of cadmium, by E. A. Partridge,<sup>1</sup> the foregoing suggestions are well exemplified. Experimentally Mr. Partridge's work appears to be excellent, and on their face his results are concordant in the highest degree. Three methods were adopted for the determinations as follows: first,

<sup>1</sup>Am. Jour. Sci., Nov. 1890, p. 377.

the ignition of  $\text{CdC}_2\text{O}_4$  to  $\text{CdO}$ ; second, the conversion of  $\text{CdSO}_4$  into  $\text{CdS}$  by heating in a stream of  $\text{H}_2\text{S}$ ; third, a similar conversion of  $\text{CdC}_2\text{O}_4$  into  $\text{CdS}$ . In each series ten experiments were made, and from each experiment individually the atomic weight of cadmium was computed. In brief, the results obtained were as follows, omitting details and taking  $\text{O} = 16$  as the standard of comparison:

	$\text{CdC}_2\text{O}_4 : \text{CdO}$ .	$\text{CdSO}_4 : \text{CdS}$ .	$\text{CdC}_2\text{O}_4 : \text{CdS}$ .
$\text{Cd} = \text{maximum,}$	111.834	111.818	111.833
minimum,	111.759	111.778	111.771
mean,	111.8027	111.7969	111.805

The mean of all is  $\text{Cd} = 111.8015$ , with an extreme range from lowest to highest of only 0.075.

Curiously, however, Mr. Partridge does not state what values he assumed for the atomic weights of carbon and sulphur in making his computations. Working back from some of his figures, I find that he must have taken the round numbers 12 and 32; and just here the question of concordance may be raised. In a recalculation of the data I have reduced all the experiments to percentage form, getting the averages of the three series into the subjoined proportions:

1st series,  $\text{CdC}_2\text{O}_4 : \text{CdO} :: 100 : 63.964 \pm .0011$ .

2d series,  $\text{CdSO}_4 : \text{CdS} :: 100 : 69.199 \pm .0012$ .

3d series,  $\text{CdC}_2\text{O}_4 : \text{CdS} :: 100 : 71.973 \pm .0007$ .

Now, when  $\text{O} = 16$ , these ratios give equations containing each an absolute term. If we compute with  $\text{C} = 12$  and  $\text{S} = 32$ , we get one set of values for  $\text{Cd}$ ; if we take Stas' figures,  $\text{C} = 12.005$  and  $\text{S} = 32.074$ , we get another set; and if we assume the factors given in my own "Recalculation of the Atomic Weights," viz.,  $\text{C} = 12.001$  and  $\text{S} = 32.058$ , we have still a third series. The results are as follows, in mean:

	$\text{C, 12.001.}$ $\text{S, 32.058.}$	$\text{C, 12.005.}$ $\text{S, 32.074.}$
1st series, $\text{Cd} =$	111.801	111.8178
2d series, $\text{Cd} =$	111.785	111.7111
3d series, $\text{Cd} =$	111.808	111.5788
Range,	.023	.2390

Hence we see clearly that the concordance between the three series of determinations is conditioned, under the ordinary modes of calculation, by the uncertainties in the factors used. If the

concordance shown by Partridge is real, Stas' values for C, or S, or both, are in error. If Stas' values are correct, then the three series of Mr. Partridge are discordant by nearly one-fourth of a unit in the atomic weight of cadmium. The small variations in the low atomic weights are multiplied in the higher figure.

In a discussion of this sort it is perhaps not possible to establish any distinct criterion of accuracy by means of which constant errors can be detected and placed. It is possible, however, at least in certain cases, to so handle data that the results of calculation shall involve no extraneous uncertainties. In the present instance the ratios measured by Partridge are capable of quite independent discussion, and by the simplest of means.

If we continue to put  $O = 16$  as our standard of comparison, and use the symbols of the elements algebraically to represent atomic weights, the three proportions given above may be transformed into the following linear equations:

$$1st \text{ series, } 36.036Cd = 127.928C + 2493.696.$$

$$2d \text{ series, } 30.801Cd = -30.801S + 4428.736.$$

$$3d \text{ series, } 28.027Cd = 143.946C - 100S + 4606.272.$$

Here we have three equations with three unknown quantities, Cd, C, and S, and no assumption need be made in advance as to the value of either. Solving directly, these equations give us the following results:

$$Cd = 111.7850$$

$$C = 11.9958$$

$$S = 32.0002.$$

These values are independent of all other determinations, and contain only the errors of Partridge's own work, divided into three portions, instead of being accumulated upon the atomic weight of cadmium alone. They involve, however, the assumption that the three sets of observations are of equal weight, which may or may not be true. If different weights are assigned we must then form normal equations by the method of least squares, and their solution might modify our final figures. For present purposes, however, the more laborious method of computation, with its discussion of weights and probable errors, is quite unnecessary. Such a discussion may be found in Strecker's recalculation of Liebig and Redtenbacher's data relative to the atomic weight of carbon.<sup>1</sup> So far as I know, that paper stands alone in chemical literature, the only one of its kind.

<sup>1</sup> Ann. Chem. (Liebig) **59**, 280 (1846).

Recurring now to the three atomic weights deduced from the three equations, we find that the values for carbon and sulphur vary slightly from the best recognised determinations. The extent of that variation may perhaps serve as an index of the accuracy of the work done, and the question of concordance of data assumes a new form. The more nearly the figures for C and S agree with established values, the better the determinations probably are; and in the present case the agreement is close enough to establish a reasonable presumption in favor of Partridge's methods. The constant errors in his work cannot be large, and they are probably all in one direction.

But between Partridge's determinations, however discussed, and the atomic weight of cadmium as measured by either Dumas or Huntington, there is a discordance of nearly half a unit. The latter chemists, both working with haloid salts of cadmium, are in close agreement; and their data, with Stas' values for Ag, Cl, and Br, and with  $O = 16$ , make Cd about 112.23, very nearly. This discordance is probably real, and due mainly to differences in experimental methods. Its cause can only be found by further experiments, and certain lines of investigation are easily suggested. Apart from the obvious plan of scrutinising each method by itself, and seeking for the constant errors which must exist on one side or the other, it is clear that new modes of determination should be attempted, lying between and connecting the existing data. For example, the ratios  $CdO : CdSO_4$ ,  $Cd : O$ ,  $Cd : S$ ,  $Cd : Ag$ ,  $Cd : Cl$ , and  $Cd : Br$  are all apparently capable of direct measurement; and they would, if determined, serve to check each other and to control the older determinations. A system of such interlacing ratios can be discussed collectively, by least squares, so as to distribute errors of observation, the constant error of any one series of data being equivalent to an accidental error in its relations to the other series. In a large system of ratios the constant errors can hardly be all in one direction, and they must tend to neutralise each other to a very considerable degree. Each ratio should contribute to our knowledge of every atomic weight involved in it, and not be considered solely with reference to a single component. The current methods of computation are fallacious in so far as they tend to magnify and accumulate errors which could be partially eliminated.



## ON BENZOQUINONECARBOXYLIC ACIDS.

BY JULIUS STIEGLITZ.

Only one compound of the group of benzoquinonecarboxylic acids is known, viz., trimethylquinonecarboxylic acid,  $(\text{CH}_3)_3\text{C}_6\text{O}_2(\text{COOH})$ , obtained by J. U. Nef<sup>1</sup> by oxidising *p*-diamidodurylic acid,  $(\text{CH}_3)_2\text{C}_6(\text{NH}_2)_2(\text{COOH})$ . All attempts to obtain such acids from their well-known and stable ethers by saponification, as well as from hydroquinonecarboxylic acids by oxidation, were unsuccessful. As yet, however, only such ethers of quinone-carbonic acids have been investigated as contain ethylated carboxylic groups directly attached to the benzene ring, and which therefore are  $\beta$ -ketonic acid ethers. As different results might be obtained with quinone compounds of the  $\gamma$ - and  $\delta$ -ketonic acid series, I began an investigation of the benzoquinone derivatives of malonic ether. A method for the preparation of these derivatives of malonic ether was suggested by the ease with which halogen atoms in certain quinone compounds had been replaced by various radicals.

*Paradichlorquinonedimalonic Ether*,  $\text{C}_6\text{Cl}_2\text{O}_2 \left( \text{CH} \begin{smallmatrix} \text{CO}_2\text{C}_2\text{H}_5 \\ \text{CO}_2\text{C}_2\text{H}_5 \end{smallmatrix} \right)_2$ ,

was prepared by treating chloranil (1 molecule) in dry benzene or acetone solution with sodium malonic ether (4 molecules) in absolute-alcoholic solution. The reaction, which takes place instantly in the cold, is completed by warming a few minutes on a water-bath. By acidifying, washing, drying and evaporating the benzene solution, a dark oil results, which deposits yellow needles when mixed with a little cold alcohol. After recrystallisation from hot alcohol, light yellow needles are obtained, which have the composition  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{O}_{10}$ .

	Calculated.		Found.	
	I.	II.	I.	II.
$\text{C}_{20}$	240	48.68	48.43	...
$\text{H}_{22}$	22	4.46	4.55	...
$\text{Cl}_2$	71	14.40	...	14.35
$\text{O}_{10}$	160	32.46	...	...
	<hr/>	<hr/>		
	493	100.00		

The proof that the two chlorine atoms replaced occupied *para* positions is given below.

<sup>1</sup>Ann. Chem. (Liebig) 237, 11.

A great many experiments were made to determine the best conditions for the reaction, but only a small yield could be obtained—in no case more than 10 per cent. of the theoretical yield. No other pure compounds could be separated from the dark mother-liquid. Dichloroquinonedimalonic ether is difficultly soluble in cold alcohol, ether or benzene, and dissolves most readily in chloroform and hot alcohol. It dissolves in sodic and potassic hydrate solution with a deep pure violet color resembling exactly a concentrated solution of potassium permanganate. The coloration is due to the formation of salts in which the remaining acid hydrogen atom of the malonic ether groups is replaced by sodium or potassium. These ether salts are rapidly saponified in the cold, as will be described below, without any change of color. With ammonia the new compound gives a deep navy-blue solution whose color disappears after some time. Reducing agents transform it into paradichlorhydroquinonedimalonic ether,



The reduction can be effected by sulphurous acid in aqueous or acetone solution, or by zinc dust and glacial acetic acid. By the latter method a green product results, from which white crystals can be obtained by recrystallising from alcohol and washing with cold ether. The white needles formed melt at 160°–161° to a perfectly colorless liquid;<sup>1</sup> they are easily soluble in alcohol, ether, benzene, etc., and in ammonia with a transient deep blue color, in fixed alkalis with a permanent dark violet color. Their composition is  $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{O}_{10}$ .

	Calculated.		Found.
	I.	II.	
$\text{C}_{20}$	240	48.48	48.30
$\text{H}_{24}$	24	4.85	4.87
$\text{Cl}_2$	71	14.34	...
$\text{O}_{10}$	160	32.33	...
	<hr/> 495	<hr/> 100.00	

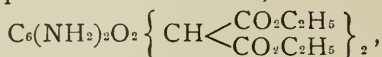
Oxidising agents, as ferric chloride, convert the hydroquinone into the quinone. Dichloroquinonedimalonic ether was further characterised by the replacement of its two chlorine atoms by amido-groups, by treating it with alcoholic ammonia in the

<sup>1</sup> In marked contrast to the analogous dichlorhydroquinoneterephthalic ether. Hantzsch, Ber. d. chem. Ges. 20, 1313.



cold. When the dark-blue coloration first formed is converted into a dark-yellow one, the reaction is finished.

Paradiamidoquinonedimalonic ether,



is precipitated when the yellow alcoholic solution is diluted with water and poured into very cold dilute sulphuric acid. The red needles obtained can be purified by dissolving them in chloroform and precipitating them with petroleic ether or simply by washing with cold ether. They melt at  $159^\circ$ – $160^\circ$  and appear as long, flat, perfect prisms when examined with a microscope. They are soluble in alkaline, but not in acid, solvents. A combustion showed that the formula  $\text{C}_{20}\text{N}_2\text{H}_{26}\text{O}_{10}$  is correct.

	Calculated.	Found.
N	6.17	6.07

*Saponification of dichlorquinonedimalonic ether.*—When this ether is suspended in an excess of dilute sodic hydrate it dissolves very quickly, and soon the smell of alcohol is unmistakably perceptible; if, after standing only a few minutes, the solution is poured into cold sulphuric acid, a brown precipitate is formed. By recrystallisation from acetone or alcohol dark-red plates are obtained, which sublime with slight decomposition and without melting, and which are easily soluble in alkalies, alcohol and acetone, less so in ether. The compound is parachlorhydroxyquinone,  $\text{C}_6(\text{OH})\text{H}_2\text{ClO}_2$ .

	Calculated.		Found.	
	I.	II.	I.	II.
C <sub>6</sub>	72	45.43	45.17	...
H <sub>3</sub>	3	1.89	2.10	...
Cl	35.5	22.39	...	22.19
O <sub>3</sub>	48	30.29	...	...
	<hr/> 158.5	<hr/> 100.00		

The relative position of the chlorine atom and the hydroxyl-group is shown by the following experiment. If, as just described, dichlorquinonedimalonic ether is dissolved in an excess of dilute alkali, the solution allowed to stand for *an hour* and then warmed for a few minutes on a water-bath, both chlorine atoms are replaced by hydroxyl-groups. The brown alkaline liquid is slowly poured into strong sulphuric acid, which is kept cold by ice so that its

temperature never rises above  $15^{\circ}$ ; if this solution is extracted with a large quantity of ether, the ether leaves upon evaporation crystals of paradihydroxyquinone.

The crystals were compared with a specimen prepared from dihydroxyquinone terephthalic ether,<sup>1</sup> and were found to be perfectly identical with Nietzki's and Löwy's paradihydroxyquinone. The compound obtained from dichlorquinonedimalonic ether sublimed between  $190^{\circ}$  and  $205^{\circ}$ ; it dissolved readily in acetic ether, from which it was obtained in the saw-edged crystals characteristic of the substance. With concentrated alkalis a red precipitate was formed, which gave with a little water a red, with more water a yellow, solution. The quinone itself had an orange color and was found to be absolutely free from chlorine. The yield was too small to make a combustion possible, but all qualitative tests agreed with the properties of paradihydroxyquinone, the formation of which is also indicated by the results obtained by analysing the chlorhydroxyquinone obtained by the same reaction. The formation of paradihydroxyquinone proves that all the compounds described are para-derivatives of benzene.

The reaction by which chlorhydroxyquinone and dihydroxyquinone are produced must consist in the replacement of the malonic groups by hydrogen; by a reaction analogous to that in the case of the replacement of the formyl rests by hydrogen in Löwy's reaction, after the chlorine atoms in dichlorquinonedimalonic had been replaced by hydroxyl groups. This unexpected result has led me to begin an investigation of the product formed by the action of sodium malonic ether on dibromquinone-terephthalic ether. As yet no definite results have been obtained in this line of investigation, and I shall only add a few words about the preparation of dibromquinoneterephthalic ether, as I could greatly simplify Herrmann's<sup>2</sup> and Böniger's<sup>3</sup> method for its preparation from succinylsuccinic ether. The latter is dissolved in dry chloroform, and bromine, in the proportion of equal molecules, gradually added; the chloroform solution is then shaken with an aqueous solution of sulphurous acid, dried and evaporated on a water-bath. The crude dihydroxyterephthalic ether obtained is dissolved in warm glacial acetic acid, and water (5-10 per cent. of the weight of glacial acetic acid used) and 3 more

<sup>1</sup> Löwy: Ber. d. chem. Ges. **19**, 2385; Böniger: Ibid. **22**, 1284; Nietzki: Ibid. **21**, 2374.

<sup>2</sup> Herrmann: Ber. d. chem. Ges. **19**, 2234.

<sup>3</sup> Böniger: Ibid. **21**, 1758.

equivalents of bromine added. This mixture is allowed to stand over night in a closed flask. Dibromquinoneterephthalic ether separates out in crystals, and more of it is precipitated by successive additions of small quantities of water. It is generally perfectly pure, but if it should contain some unchanged dihydroxyterephthalic ether, it can be easily purified by dissolving in a small quantity of hot glacial acetic acid, cooling, and adding some water and a little bromine. A second method consists in dissolving the succinylosuccinic ether directly in glacial acetic acid and treating with bromine and water in one operation; it is advisable then to add the water only after about a third of the bromine has been already used. 30 grams of succinylosuccinic ether gave, by the first method, 40.5 grams of pure dibromquinoneterephthalic ether (84.5 per cent. of the calculated quantity); and 10 grams gave, by the second method, 13.2 grams of the dibrom-compound (82.5 per cent. of the theoretical yield). Professor Nef proposed to me to try new methods for making benzoquinonecarboxylic acids, and helped me by his advice, which I wish here to acknowledge with thanks.

CHEMICAL LABORATORY, CLARK UNIVERSITY.

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Contributions from the Chemical Laboratory of Wesleyan University.

## IX.—THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.

BY W. O. ATWATER AND C. D. WOODS.

REPORTED BY W. O. ATWATER.

[Continued from page 547, Vol. 12.]

### *Loss of Nitrogen.*

In many of the experiments, instead of gain of nitrogen, a decided loss was observed. With peas, the loss appears in every case in which there were no root tubercles, and in many of the cases in which only a "few" tubercles were developed. (See Table 4 above, and detailed tables at end of this article.) This loss of nitrogen manifested itself whether the plants were fed with nitrogen

or not, though it was larger with the nitrogen-fed plants than those which received no nitrates.

With the oats and corn (see Tables 1 and 2 above, and detailed tables at the end of article), most of the nitrogen-fed plants showed a large loss, while with those which had no nitrates there was a slight gain.

Two sources of loss of nitrogen suggest themselves, namely, decomposition of the organic matter of seed or plant, and decomposition of nitrates fed. Loss from decomposition of seed, or of seed and plants, accords with the results of observations in experiments at this place, from the report<sup>1</sup> of which the following table is copied. In each of the thirteen experiments, from five to twenty-three peas were germinated in a germinating apparatus or in sand, and allowed to grow for a longer or shorter period in water or sand without artificial food supply. The difference between the nitrogen in the seed and that found at the end of the experiment in the plants and the medium in which they grew is the nitrogen lost.

*Experiments on the Loss of Nitrogen during Germination and Early Growth.*

Conditions of Germination and Growth of Peas.	Experiments.		Time of germination and growth.	Nitrogen lost in per cent. of total in seed at beginning of experiments.	
	Series.	No.			
<i>Water Culture.</i>					
Seeds germinated and then suspended with roots immersed in pure water. Experiments in open air, . . . }	III. {	3 1 2	8 days. 10 15	8.4 per cent. 9.8 1.5	
<i>Sand Culture.</i>					
Seeds germinated and grown in sand. Experiments in open air, . . . }	IV. {	6 7 8	6 10 14	5.9 10.6 15.1	
Seeds germinated and then transferred to sand,	{ Experiments in greenhouse, }	V. {	9	18	7.3
			10	28	12.4
			11	52	16.3
	{ Experiments in dwelling-house, }	VI. {	12	29	8.2
			13	42	11.0

<sup>1</sup> On the Loss of Nitrogen by Plants during Germination and Growth: W. O. Atwater and E. W. Rockwood, this Journal 8, 327.

The results thus cited indicate that germination and early growth of peas are, or at any rate may be, accompanied by greater or less loss of nitrogen. In the experiments herewith reported upon there was an average loss of about 9 milligrams of nitrogen with the peas (Series VII and IX) which were not nitrogen-fed and which failed to develop root tubercles. In the peas of Series VII and IX which were fed with nitrates there was an average loss of about 23 milligrams in the plants without root tubercles. The loss with the nitrogen-fed peas was two and one-half times as great as with those not nitrogen-fed.

With oats and corn, fed with very little or with no nitrogen, there is no apparent loss, but a small gain instead. On the other hand, with the nitrogen-fed oats and corn the loss of nitrogen is marked, increases with the quantity of nitrogen supplied, and is much larger than with the peas.

This loss of nitrogen gives added force to the suggestion made in the report<sup>1</sup> of the earlier work here, that if nitrogen escaped in some of the trials it may have done so in the other cases as well. If this be true the results are all inaccurate as indications of the actual atmospheric nitrogen acquired, and the plants must really have obtained more nitrogen than the figures here imply.

These experiments do not tell to what extent the loss observed with the oats and corn and with the peas which had no root tubercles, was from the seed and to what extent from the nitrates; whether, as would seem most likely, it was due to the action of microbes; or what connection there may be between plants of different species and the loss of nitrogen. These and kindred questions must remain for future research to decide.

### *Acquisition of Nitrogen from the Air.*

That the legumes experimented with obtained large amounts of nitrogen from the air is abundantly shown by the facts cited in the tables. The evidence coincides exactly with that of the previous experiments here and the later ones by Hellriegel and others, and is plain and unmistakable. Peas of a small, early variety (East Hartford Early), grown in sand, with no nitrogenous food except that in the seed and what they were able to acquire from the atmosphere, attained a height of over five feet. With nitrogen supplied in the nutritive solutions they reached a height of over

<sup>1</sup> Loc. cit. p. 403.



eight feet. The quantities of atmospheric nitrogen obtained by the pea and alfalfa plants (Tables 3, 4 and 5 above) were in many cases very large.

Whether the nitrogen thus obtained from the air was free or combined nitrogen these experiments do not absolutely prove. But the quantities obtained are so very large as to leave little doubt that it is free nitrogen. That any considerable quantity of combined nitrogen could have been taken from the atmosphere by the nutritive solutions and soil, and thus conveyed to the plants, would seem from the consideration cited in connection with the descriptions of "blank" tests above, to be out of the question, nor does it seem at all reasonable to assume the possibility of so much combined nitrogen being absorbed by the foliage of the plants.<sup>1</sup> The experiments of Hellriegel already referred to, in which plants grown in confined air without combined nitrogen, but with root tubercles, acquire considerable quantities of nitrogen, would seem to put the acquisition of free nitrogen by plants beyond question. This special subject, however, demands further investigation. Plans for its study are now being made.

One special point calls for notice here. In general, the smaller plants with fewer seeds show a loss of nitrogen, while the larger, stronger plants with more normal development show the gain. In many of the experiments which demonstrated the gains of nitrogen, some of the plants were large and had a number of well-developed seeds, while others were small and had few seeds. The natural inferences are that the gain of nitrogen was made by the well-developed plants; that the actual gain was larger than the apparent gain; and that this actual gain by the well-developed plants covered the apparent gain in the whole experiment *plus* enough to make up for any losses from decomposition of seeds of both the vigorous and the weaker plants, from decomposition of nitrates, and from other causes. In other words, it seems probable that the vigorous plants had to make up for the losses of the weaker ones, and hence the actual gain by normal plants is larger than the statistics of these experiments show.

Thus in the experiments with East Hartford Early Peas it was observed that, as a rule, unless the plants not supplied with nitrates made a growth of at least 14 inches and developed more

<sup>1</sup> See discussion of this subject in description of previous experiments in this place, this Journal 6, 378.

than one pea to a vine, the pea was a small one, and the results indicated a loss of nitrogen. The following data from Table 9 will serve as illustrations:

No. 120—1 plant, 15 inches high; 1 pod, 1 pea; loss, 7.7 mg. nitrogen.

No. 128—3 plants, 12 inches high; 3 pods, 3 peas; loss, 3.6 mg. nitrogen.

No. 137—3 plants, 10–15 inches high; 1 pod, 1 pea; loss, 11.4 mg. nitrogen.

No. 138—4 plants, 12–27 inches high; 2 pods, 2 peas; loss, 3.9 mg. nitrogen.

No. 140—4 plants, 9.12 inches high; 4 pods, 4 peas; loss, 2.4 mg. nitrogen.

In only one case (No. 127; 3 plants, 12–15 in. high; 3 pods, 3 peas; gain, 26.5 mg. nitrogen) did the plants not nitrogen-fed show a gain without producing more than an average of one pea per vine. In this case the 15-inch plant had two peas, and it seems at least reasonable to question whether this plant did not make the gain.

In nearly all, if not all, of the experiments with East Hartford Early Peas that have shown a gain of nitrogen, some of the plants have been small and with no peas, or at most only one. It seems reasonable to suppose from the above-cited trials that the apparent gain may have been due to the large, strong plants, and that these latter gained enough to offset the loss by the weaker plants and provide, in addition, for the apparent gain of the whole experiment. The following from table above cited will illustrate.

No. 136 had four plants; three 14 inches and one 58 inches high and bearing 5 pods with 12 peas. The estimated gain of nitrogen was 242.9 milligrams. In this case the three 14-inch plants bore 3 pods with 3 peas, and the large plant 2 pods with 9 peas. The loss almost uniformly observed with the small plants bearing few peas in other experiments, makes it possible that the small plants did not hold their own; that, in other words, taken by themselves they lost nitrogen. If this be so, the gain of at least one-fourth of a gram must have been made by the one large plant. The same may be said of No. 135. Two of the plants were small and bore practically no fruit. The apparent gain was about one-fifth gram. The inference is that the well-developed plants made the whole gain of nitrogen. In most of the experiments there was



more or less of this difference of growth, and to distribute the gain evenly to all of the plants of a single experiment would obviously be erroneous. Indeed, there is little room for doubt that the apparent gain of the large plants would have been materially greater than that of the whole experiment, if the weak plants had not been present.

Why, in the same pot, under apparently the same conditions, one plant should thrive so much better than others; why one should grow luxuriantly while others starve, is difficult to understand. That this was the case in the experiments with East Hartford Early Peas is evident. The growth of Champion of England Peas has been much more uniform. The different plants in the same pot differ but little from each other in apparent vigor of growth.

The plan for the next experiments here will include pots with only one plant in each, and thus eliminate the difficulties noticed in the experiments with East Hartford Early Peas, and to a greater or less extent in those with other plants.

*Species of Plants which acquire Atmospheric Nitrogen in Large Quantities.*

In our experiments, peas and alfalfa have gained large quantities of nitrogen from the air. The corn in Series IX acquired small quantities of nitrogen from the air, but this acquisition was not substantiated with experiments of corn and oats of Series XII and XIII. The reasons for this difference of results with the corn and oats demand further experiment for their explanation.

Hellriegel,<sup>1</sup> Wolff,<sup>2</sup> Bréal,<sup>3</sup> Lawes and Gilbert,<sup>4</sup> and others have found peas, lupines, serradella, beans, and, in all probability, clover and other legumes to acquire atmospheric nitrogen, while the cereals, buckwheat and potatoes, have failed to give positive evidence of so doing. The facts thus attested accord with manifold observations of field practice in implying that leguminous plants, or at least some species of legumes, possess in high degree the power to obtain nitrogen from the air.

*Relation between Root Tubercles and Gain of Nitrogen.*

Examination of the detailed tabular statements of results of 80 experiments with peas and alfalfa here described shows that in

<sup>1</sup> Loc. cit.

<sup>3</sup> Compt. rend. 109, 670.

<sup>2</sup> Landw. Jahrb. 1887, 659.

<sup>4</sup> Loc. cit.

every case, without exception, where there were no root tubercles there was loss of nitrogen; where there were "few" tubercles there was sometimes a slight loss of nitrogen, at other times a slight gain; with a "fair number" of tubercles there was a decided gain; where there was a "large number" of tubercles the gain of nitrogen was very large.

In the experiments with corn and oats, which had no tubercles, there was, in a few cases, a very slight gain of nitrogen, in others a loss, generally very large. The explanation of this behavior of the cereal plants must await further investigation. Meanwhile it is sufficient to say the leguminous plants have root tubercles and acquire large quantities of nitrogen.

The nature and functions of root tubercles, though now actively discussed, are not fully understood. While there is as yet no absolute proof that the root tubercles or the microbes which appear to be connected with them are the cause of the gain of nitrogen, the fact that there is a connection between the root tubercles and the amount of nitrogen acquired by the plants from the air is unmistakable.

It seems probable that this relation holds in field as in pot culture. The past season the Station grew half an acre of cow-peas, which yielded at the rate of about eight tons of green fodder per acre. In some ten different places in the field the roots were examined and found to be covered with tubercles of considerable size. Some were as large as peas. At one end of the field, where the yield was relatively light, the roots had less tubercles than elsewhere; and in general where the growth was heaviest, the tubercles seemed to be most abundant.

Our experiments thus confirm the important observation, first made by Hellriegel, of the connection between root tubercles and acquisition of nitrogen, and support the belief that the faculty of obtaining atmospheric nitrogen is especially characteristic of some, if not all, species of legumes.

#### *Relation between Soil Infusions and Root Tubercles.*

As may be seen from Table 6, herewith, the addition of soil infusion seemed to make infection much more certain, but a large number of the plants had an abundance of root tubercles without the infusions, although grown in sterilised sand supplied with water that had been distilled, and solutions prepared with that

water. That this should be the case is not at all surprising if, as seems probable, the development of the tubercles is due to bacteria or other micro-organisms. These experiments were conducted near cultivated ground, a garden, where such organisms or their germs might naturally be abundant in the air and find their way to the pots in which the plants were cultivated.

A possible explanation of this greater abundance in the nitrogen-fed plants may be that these plants are sustained by the nitrogen supplied until they become infected and are enabled to attain the nitrogen from the air.

TABLE 6.

*Relation between Soil Infusion and Tubercles.*

NUMBERS OF EXPERIMENTS IN WHICH THERE WERE NO ROOT TUBERCLES, A FEW, A FAIR NUMBER, OR A LARGE NUMBER, AS ESTIMATED AT HARVESTING.

	Champion of England Peas, Series VII, 1888.	Alfalfa, Series VIII.	East Hartford Early Peas, Series X, 1889.	Champion of England Peas, Series XI, 1889.	Total No. of Experiments.	Per Cent. of Total No. of Experiments.
<i>Without Soil Infusion.</i>						
Experiments with no tubercles, . . . .	2	...	1	2	5	15.6
“ “ few tubercles, . . . .	2	2	2	2	8	25.0
“ “ fair number of tubercles, . . . .	1	...	2	1	4	12.5
“ “ large number of tubercles, . . . .	1	...	11	3	15	46.9
Total number of experiments, . . . .	6	2	16	8	32	100.0
<i>With Soil Infusion.</i>						
Experiments with no tubercles, . . . .	0	...	1	0	1	2.7
“ “ few tubercles, . . . .	2	1	9	1	13	35.1
“ “ fair number of tubercles, . . . .	2	1	2	2	7	18.9
“ “ large number of tubercles, . . . .	4	1	6	5	16	43.3
Total number of experiments, . . . .	8	3	18	8	37	100.0

Table 6 recapitulates the results of 69 experiments, 64 with peas (those with bacteria cultures are omitted) and 5 with alfalfa. The first group contains 32 experiments with peas and alfalfa, to which no soil infusions were added. The last column shows the per-

centage of experiments in which tubercles were found at harvest. The plants in 47 per cent. of the experiments had a "large number" of tubercles, notwithstanding they received no soil infusion. The second group contains 37 experiments with alfalfa and peas, all of which were treated with soil infusion. In only 43 per cent of these were a "large number" of tubercles found.

#### SUMMARY.

The results of the experiments above described, and the conclusions drawn from them and from the other investigations referred to, may be briefly summarised as follows:

1. In the previous experiments at this place (made in 1881-2 and published in 1882, 1884 and later), peas were shown to obtain large quantities of nitrogen from the air during the period of growth. The conditions were such as to make it extremely probable that the free nitrogen of the air was thus assimilated.

2. Later experiments by Hellriegel and others have confirmed the results thus obtained with peas; have shown similar acquisition of nitrogen from the air by serradella, lupine, clover and other legumes; have strongly confirmed the assimilation of free nitrogen, and have shown a connection between root tubercles and the acquisition of atmospheric nitrogen.

3. The experiments here described still further confirm the acquisition of atmospheric nitrogen by peas, and show that the same is done by alfalfa.

4. In the eighty-nine experiments here reported, there was in no case any large gain without root tubercles, but with them there was uniformly more or less gain of nitrogen from the air. As a rule, the greater the abundance of root tubercles, the larger and more vigorous were the plants and the greater was the amount of atmospheric nitrogen acquired. The connection between root tubercles and the acquisition of nitrogen, which was first pointed out by Hellriegel, is abundantly confirmed. What this connection is; what are the relations of micro-organisms to the root tubercles and to the acquisition of nitrogen; and in general how the nitrogen is obtained, are questions still to be solved.

5. In the experiments here reported the addition of soil infusions did not seem necessary for the production of root tubercles. A plausible supposition is that the micro-organisms or their spores were floating in the air and were deposited in the pots in which the plants grew.

6. The cereals here experimented with did not manifest this power of acquiring nitrogen, nor did they have such tubercles as are formed on the roots of legumes. These results accord with those obtained elsewhere, except in the fact that in some of the trials very small quantities of nitrogen were apparently acquired from the air. What importance, if any, is to be attached to this observation it is not easy to say.

7. In a number of these experiments, as in similar ones previously reported, there was a loss of nitrogen instead of gain. The loss occurred where there were no root tubercles; it was especially large with oat and corn plants, and largest where they had the most nitrogen at their disposal in the form of nitrates. This loss may probably be due to the decomposition of the seeds and nitrates through the agency of micro-organisms.

8. The failure of earlier experiments to bring evidence of the acquisition of nitrogen from the air may very probably be due in part to this loss of nitrogen, but more especially to the precautions for excluding compounds of nitrogen, which precautions were likewise calculated to exclude the action of microbes, electricity, or both, by the aid, or at least in the presence, of which the nitrogen is assimilated.

In brief, the acquisition of large quantities of atmospheric nitrogen by leguminous plants, which was first demonstrated by experiments here and has been since confirmed by others, is still further confirmed by the experiments herewith reported. These experiments in like manner confirm the observation of the connection between root tubercles and the acquisition of nitrogen. There is scarcely room for doubt that the free nitrogen of the air is thus acquired by plants.

# APPENDIX.

The detailed results of the experiments described above are condensed in Tables I-VII which follow.

TABLE I.—*Series VII, 1888. Champion of England Peas.*

## CONDENSED STATISTICS.

No. of Experiment.	Kilos. of Sand.	Weight of Seed.	Nitrogen Supplied.			Soil Infusions.	Water added during Growth.	Root Tubercles at Harvest.	Mature Plants.				Nitrogen at End of Experiment.			Gain (or Loss —) of Nitrogen.
			In Seed.	In Nutrients.	Total.				Number.	Weight.			In Plants.	In Nutrients.	Total.	
										Tops.	Roots (and Sand).	Total.				
81	2.8	1111.5	Mg. 48.9	Mg. 48.9	Mg. 48.9	Cc. ...	Cc. 700	None.	3	G. 2.26	G. 1.06	G. 3.32	Mg. 41.9	Mg. ...	Mg. 41.9	Mg. -7.0
82	2.8	1048.5	46.1	...	46.1	...	600	Few.	3	1.03	2.07	3.10	44.4	...	44.4	-1.7
83	2.8	1059.0	46.6	...	46.6	25	900	Fair number.	3	2.78	2.55	5.33	132.2	...	132.2	85.6
84	2.8	1020.5	44.9	...	44.9	25	900	Large number.	3	2.64	1.79	4.43	161.6	...	161.6	116.7
86	2.8	1047.5	46.1	75.9	122.0	...	1000	Fair number.	3	2.55	5.75	8.30	138.1	24.8	162.9	40.9
87	2.8	979.9	43.1	75.9	119.0	25	1100	Few.	3	2.59	4.18	6.77	136.3	25.6	161.9	42.9
88	2.8	1054.0	46.4	75.9	122.3	25	800	Fair number.	3	2.30	1.81	4.11	124.6	24.2	148.8	26.5
89	2.8	1090.5	47.9	151.8	199.7	...	600	Few.	3	2.21	2.37	4.58	122.3	57.2	179.5	-20.2
91	2.8	1064.0	46.8	151.8	198.6	25	1100	Large number.	3	3.30	2.00	5.30	216.5	64.0	280.5	81.9
92	2.8	1030.0	45.3	151.8	197.1	25	1000	Large number.	3	2.93	1.31	4.24	183.6	69.4	253.0	55.9
93	6	1070.0	47.1	113.8	160.9	...	1300	None.	3	3.07	5.16	8.23	135.0	17.0	152.0	-8.9
94	6	1031.5	45.4	113.8	159.2	...	1700	Fair number.	3	2.56	1.20	3.76	122.8	28.2	151.0	-8.2
95	6	1063.5	46.8	113.8	160.6	25	1700	Large number.	3	2.31	1.27	3.58	131.6	38.1	169.7	9.1
96	9	969.5	42.7	113.8	156.5	25	900	Few.	3	.68	.84	1.52	44.7	95.0	139.7	-16.8



97	3	684.5	30.1	10.8	40.9	Bacteria Cultures	1800	None.	2	.98	2.06	3.04	37.1	...	37.1	-3.8
98	3	679.5	29.9	10.8	40.7	5	1900	None.	2	.90	.82	1.72	35.4	...	35.4	-5.3
99	3	627.0	27.6	10.8	38.4	5	1800	None.	2	.84	.56	1.40	22.8	...	22.8	-15.6
100	3	633.5	27.8	10.8	38.7	5	1800	None.	2	.54	.38	.92	23.7	...	23.7	-15.0
102	3	673.5	29.6	10.8	40.4	5	1700	None.	2	.70	.94	1.64	28.0	...	28.0	-12.3
103	3	620.0	27.3	86.6	113.9	5	1900	None.	2	1.38	.40	1.78	66.6	25.5	92.1	-21.8
104	3	673.5	29.6	86.6	116.3	5	1900	None.	2	1.97	1.18	3.15	83.7	2.2	85.9	-30.4
105	3	662.5	29.2	86.6	115.8	5	1800	None.	2	1.55	1.02	2.57	87.2	15.4	102.6	-13.2
106	3	668.5	29.4	86.6	116.1	5	1900	None.	2	2.36	2.47	4.81	97.6	...	97.6	-18.5
107	3	688.5	30.3	86.6	116.9	5	1700	None.	2	1.32	.47	1.79	64.8	8.6	73.4	-43.5
108	3	659.5	29.0	86.6	115.7	5	1700	Few.	2	2.05	2.62	4.67	97.5	...	97.5	-18.2

EXPLANATION OF TABLE.—The experiments of this series may be divided into three distinct groups. The pots of the first group (Nos. 81-92) held 2.82 kilograms of sand; those of the second (Nos. 93-96), 6 kilograms; and those of the third (Nos. 97-108), 3 kilograms of sand.

In the first group, three experiments (Nos. 81-84) were without addition of nitrogen other than that in the seed; the plants in three others (Nos. 86-88) had a small amount of nitrogen, and those in the remaining three (Nos. 89-92) a larger proportion of nitrogen in the form of nitrates. The solution in which the plants of the second group (Nos. 93-96) were grown contained a small proportion of nitrogen as nitrates, though the larger amount of sand, and consequently of nutritive solution, made the actual amount of nitrogen added larger than in Nos. 86-88. In six experiments of the first group and two of the second 25 cc. of pea-soil infusion, *i. e.*, infusions from a garden soil in which peas were growing, were added to each solution. In the experiments of the third group pure cultures of bacteria, from infusions of pea soil in a solution of peptone and beef extract, were added. The nitrogen contained in the culture medium when inoculated was 10.8 milligrams. Five of the pots (Nos. 97-102) were not treated with nitrates, and six (Nos. 103-108) received each 74.8 milligrams of nitrogen as nitrates in addition to that of the seed and the culture medium.

The weight of the roots is increased by a small amount of adhering sand.

TABLE II.—Series X, 1889. *East Hartford Early Peas.*

## CONDENSED STATISTICS.

No. of Experiment.	Kilos. of Sand.	Weight of Seed.	Nitrogen Supplied			Soil Infusions.	Water added during Growth.	Duration of Growth.	Root Tubercles at Harvest.	Mature Plants.						Nitrogen at End of Experiment.			Gain (or Loss—) of Nitrogen.
			In Seed.	In Nutritive Solutions.	Total.					Height.	Number of Pods.	Number of Peas.	Weight.			In Plants.	In Nutritive Solutions.	Total.	
													Vines and Fruit.	Roots (and Sand).	Total.				
115	1	Mg. 511 486	Mg. 20.4 19.4	Cc. 1600 1525	Days 75 75	Large number. Few.	2 1	15, 20,	G. 1.37 .92	G. .67 .22	G. 2.04 1.14	Mg. 33.0 25.4	Mg. 33.0 25.4	Mg. 12.6 6.0					
116	1	486	19.4	1525	75	Few.	1	20,	.92	.22	1.14	25.4	25.4	6.0					
117	$\frac{3}{4}$	487	19.5	1575	80	Large number.	2	16, 32	1.66	.43	2.09	48.7	48.7	29.2					
118	$\frac{3}{4}$	483	19.3	1375	75	Few.	2	12, 16	.77	.25	1.02	23.8	23.8	4.5					
119	1	526	21.0	1675	75	Large number.	3	18, 18	1.57	.51	2.08	52.5	52.5	31.5					
120	1	480	19.2	1400	75	None.	1	15,	.41	.25	.66	11.5	11.5	-7.7					
123	1	491	19.6	2150	75	Few.	2	24, 30	3.90	.55	4.45	100.2	100.2	4.7					
124	1	486	19.4	2000	70	Few.	3	24, 27	3.73	.68	4.41	90.9	90.9	-4.4					
125	1½	706	28.2	2250	75	Large number.	3	2, 12, 15	1.00	.65	1.65	30.7	30.7	2.5					
126	1½	726	29.0	2350	75	Large number.	4	6, 15, 15	2.19	.74	2.93	69.5	69.5	40.4					
127	1½	744	29.8	2350	75	Large number.	3	12, 12, 15	1.82	.65	2.47	56.3	56.3	26.5					
128	1½	767	30.7	2150	70	Few.	3	12, 12, 12	1.45	.55	2.00	27.1	27.1	-3.6					

129	1 1/2	770	30.8	129.0	159.8	...	4900	84	Large number.	322, 27, 48	412	7.85	1.07	8.92	186.2	7.8	194.0	34.2
130	1 1/2	758	30.3	129.0	159.3	...	5450	97	Fair number.	323, 54, 81	3	7	.94	8.11	153.2	18.7	171.9	12.6
131	1 1/2	745	29.8	129.0	158.8	...	5900	99	Large number.	235, (27, 86) <sup>1</sup>	5	12	1.05	12.03	202.2	1.9	204.1	45.3
132	1 1/2	788	31.5	75.9	107.4	...	3250	69	Few.	314, 21, 27	4	13	1.20	6.48	99.1	4.7	103.9	-3.6
133	1 1/2	776	31.0	129.0	160.0	40	5600	97	Large number.	3 (9, 22) <sup>1</sup> , 30, 84	8	23	1.03	12.63	277.1	1.7	278.8	118.8
134	1 1/2	710	28.4	75.9	104.3	40	3200	69	Few.	315, 24, 27	5	13	1.58	6.54	102.9	...	102.9	-1.4
135	3	998	39.9	...	39.9	...	6600	90	Large number.	414, 14, 30, 62	9	25	1.27	9.24	237.1	...	237.1	197.2
136	3 1/2	940	37.6	...	37.6	...	7600	127	Large number.	414, 14, 14, 58	5	12	7.06	3.74	280.5	...	280.5	242.9
137	2 1/2	958	38.3	...	38.3	...	3250	75	None.	310, 15, 15	1	1	.97	1.55	26.9	...	26.9	-11.4
138	3	1013	40.5	...	40.5	50	3350	75	Few.	412, 12, 15, 27	2	2	1.42	1.12	2.54	...	36.6	-3.9
139	3	970	38.8	...	38.8	50	5050	113	Fair number.	413, 15, 15, 44	4	6	2.81	.65	3.46	...	67.5	28.7
140	2 1/2	981	39.2	...	39.2	50	3250	70	Fair number.	49, 12, 12, 12	4	4	1.57	1.20	2.77	...	36.8	-2.4
141	3	1006	40.2	113.8	154.1	...	7600	113	Fair number.	418, 24, 52, 54	6	16	8.53	3.31	11.84	2.1	156.8	2.7
142	3	1001	40.0	113.8	153.9	...	6000	83	Large number.	418, 22, 26, 72	9	25	11.62	2.17	13.79	...	273.2	119.3
143	3	1023	40.9	113.8	154.7	...	4700	75	Large number.	424, 27, 27	6	13	5.98	1.57	153.0	3.7	156.7	1.9
144	3	973	38.9	113.8	152.7	50	5000	75	Few.	322, 22, 22, 22	4	13	6.05	2.20	140.9	2.5	143.4	-9.3
145	2 1/2	975	39.0	113.8	152.8	50	5800	83	Large number.	418, 30, 78	9	28	9.98	1.33	11.31	...	196.5	43.7
146	3	952	38.1	113.8	151.9	50	5700	83	Fair number.	310, 15, 30, 30	7	18	6.85	1.82	211.1	4.6	215.7	63.8
147	3 1/2	1005	40.2	227.6	267.8	...	5600	70	Few.	421, 27, 27, 27	8	18	9.10	2.80	221.8	26.4	248.2	-19.6
148	3 1/2	1046	41.8	227.6	269.4	...	10400	127	Large number.	430, 30, 41, (102, 102) <sup>1</sup>	4	11	14.88	3.27	18.15	5.3	414.6	145.2
149	3 1/2	1017	40.7	227.6	268.3	50	9100	99	Large number.	424, 33, 84 (18, 96) <sup>1</sup>	11	26	15.00	2.80	17.80	1.6	261.8	-6.5
150	3 1/2	954	38.2	227.6	265.8	50	8200	97	Large number.	416, 35, 42, 83	11	24	12.40	3.60	16.00	32.9	352.0	87.2

<sup>1</sup> One of the plants had two branches of the heights given.

EXPLANATION OF TABLE.—This series includes three groups of experiments, Nos. 115-124, with  $\frac{3}{4}$  or 1 kilogram of sand; Nos. 125-134, with  $\frac{1}{4}$  kg., and Nos. 135-150, with  $2\frac{1}{2}$ , 3 or  $3\frac{1}{2}$  kilograms of sand. The plants of Nos. 115-120 were grown without addition of nitrogen other than in seed; three of them were with pea-soil infusion and three without. The other two of the first group, Nos. 123 and 124, were treated with a small proportion of nitrogen as nitrates and with pea-soil infusion. The next group was planned to include four experiments, Nos. 125-128, without nitrogen, and six, Nos. 129-134, with a relatively large proportion of nitrogen as nitrates. Half received pea-soil infusion, Nos. 132 and 134, however, finished their growth (see column 6, "Duration of growth") before the second addition of nitrates, and they consequently had a smaller proportion of nitrogen than the others of this group which had nitrates. In the third group, five, Nos. 141-146, had a small proportion of nitrates, and five, Nos. 136-140, had none. Nine of this group were treated with pea-soil infusion.

TABLE III.—Series XI, 1889. *Champion of England Peas.*

CONDENSED STATISTICS.

No. of Experiment.	Kilos. of Sand.	Weight of Seed.	Nitrogen Supplied.			Soil Infusions.	Water added during Growth.	Duration of Growth.	Root Tubercles at Harvest.	Mature Plants.							Nitrogen at End of Experiment.			Gain (or Loss) of Nitrogen.
			In Seed.	In Nutritive Solutions.	Total.					Number.	Extremes of Height.	Number of Pods.	Number of Peas.	Weight.			In Plants.	In Nutritive Solutions.	Total.	
														Vines and Fruit.	Koots (and Sand).	Total.				
151		Mg. 3 1581	Mg. 72.3	Mg. ...	Mg. 72.3	Cc. ...	Cc. 4200	Days 78	None.	4	25-34	3	2	G. 3.37	G. 1.68	G. 5.05	Mg. 62.4	Mg. ...	Mg. 62.4	Mg. -9.9
152		Mg. 3 1554	Mg. 70.9	Mg. ...	Mg. 70.9	Cc. ...	Cc. 4300	Days 78	None.	2	36-39	4	2	G. 3.03	G. 2.25	G. 5.28	Mg. 62.8	Mg. ...	Mg. 62.8	Mg. -8.1
153		Mg. 3 1564	Mg. 71.5	Mg. ...	Mg. 71.5	Cc. ...	Cc. 4400	Days 79	Few.	4	32-40	3	3	G. 2.69	G. 1.26	G. 3.95	Mg. 58.0	Mg. ...	Mg. 58.0	Mg. -13.5
154		Mg. 3 1553	Mg. 71.0	Mg. ...	Mg. 71.0	Cc. 50	Cc. 4700	Days 85	Fair number.	4	36-46	6	8	G. 5.72	G. 2.45	G. 8.17	Mg. 145.8	Mg. ...	Mg. 145.8	Mg. 74.8
155		Mg. 3 1603	Mg. 73.3	Mg. ...	Mg. 73.3	Cc. 50	Cc. 4800	Days 85	Large number.	4	44-50	5	8	G. 5.99	G. 2.74	G. 8.73	Mg. 151.9	Mg. ...	Mg. 151.9	Mg. 78.7
156		Mg. 3 1646	Mg. 75.2	Mg. ...	Mg. 75.2	Cc. 50	Cc. 4700	Days 85	Fair number.	4	32-48	5	8	G. 5.42	G. 1.72	G. 7.14	Mg. 139.1	Mg. ...	Mg. 139.1	Mg. 63.9
157		Mg. 3 1543	Mg. 70.7	Mg. 151.8	Mg. 222.5	...	Cc. 7500	Days 83	Fair number.	4	44-51	8	14	G. 12.47	G. 7.96	G. 20.43	Mg. 282.7	Mg. ...	Mg. 282.7	Mg. 60.2
158		Mg. 3 1536	Mg. 70.2	Mg. 151.8	Mg. 222.0	...	Cc. 7000	Days 85	Large number.	4	54-62	10	16	G. 14.52	G. 3.84	G. 18.36	Mg. 343.8	Mg. 3.8	Mg. 347.6	Mg. 125.6
159		Mg. 3 1541	Mg. 70.7	Mg. 151.8	Mg. 222.6	...	Cc. 7800	Days 85	Large number.	4	48-64	9	18	G. 14.38	G. 4.67	G. 19.05	Mg. 340.0	Mg. 2.0	Mg. 342.0	Mg. 119.4
160 <sup>1</sup>		Mg. 3 1552	Mg. 70.9	Mg. 151.8	Mg. 222.7	50	Cc. 8000	Days 85	Large number.	4	42-60	9	22	G. 14.95	G. 4.00	G. 18.95	Mg. 411.4	Mg. ...	Mg. 411.4	Mg. 188.7
161		Mg. 3 1588	Mg. 72.6	Mg. 151.8	Mg. 224.3	50	Cc. 7900	Days 85	Few.	4	42-54	8	15	G. 10.95	G. 2.08	G. 13.03	Mg. 236.8	Mg. 2.0	Mg. 238.8	Mg. 14.5
162		Mg. 3 1643	Mg. 75.0	Mg. 151.8	Mg. 226.8	50	Cc. 8000	Days 85	Large number.	4	42-62	8	16	G. 12.62	G. 3.52	G. 16.14	Mg. 284.9	Mg. ...	Mg. 284.9	Mg. 58.1
163		Mg. 6 2405	Mg. 109.9	Mg. 447.7	Mg. 557.6	...	Cc. 12500	Days 85	Few.	6	48-68	16	31	G. 25.52	G. 9.56	G. 35.08	Mg. 593.6	Mg. 2.4	Mg. 596.0	Mg. 38.4
164 <sup>2</sup>		Mg. 6 2241	Mg. 102.4	Mg. 447.7	Mg. 550.1	...	Cc. 13000	Days 85	Large number.	6	48-68	18	30	G. 27.67	G. 10.75	G. 38.42	Mg. 672.7	Mg. 20.5	Mg. 693.2	Mg. 143.1
165 <sup>3</sup>		Mg. 6 2300	Mg. 105.1	Mg. 447.7	Mg. 552.8	50	Cc. 13900	Days 85	Large number.	6	44-70	15	34	G. 24.85	G. 7.87	G. 32.72	Mg. 694.5	Mg. 23.5	Mg. 718.0	Mg. 165.2
166 <sup>4</sup>		Mg. 6 2286	Mg. 104.5	Mg. 371.8	Mg. 476.3	50	Cc. 8900	Days 54	Large number.	6	42-64	...	...	G. 17.27	G. 6.67	G. 23.94	Mg. 618.2	Mg. 105.5	Mg. 723.7	Mg. 247.4

<sup>1</sup> 8 peas eaten by birds.<sup>2</sup> 1 pea eaten by birds.<sup>3</sup> 3 peas eaten by birds.<sup>4</sup> Growth stopped when plant was in full bloom.

EXPLANATION OF TABLE.—In this series the plants in one group of six pots (Nos. 157-156) were grown without addition of nitrogen other than that in the seed. In six pots (Nos. 157-162) a small proportion, and in four pots (Nos. 163-166) a larger proportion of nitrogen was added in the form of nitrates. Half of these groups were treated with 50 cc. of pea-soil infusion. In the column "Extremes of Height," the height of the shortest and of the tallest plant in each pot is given. The weight of "Koots" and "Total" includes a small and varying amount of adhering sand, which it was not practicable to remove. When about half-grown, some of the peas of the plants in Nos. 160, 164 and 165 were eaten by birds. No correction for the nitrogen thus lost is made, so the calculated gain in the last column is less than the actual gain. Anis attacked No. 166 when the plants were in blossom. The attempt to drive them out with a small quantity of borax was successful, but the plants were killed thereby.

TABLE IV.—*Series VIII, 1888-89. Alfalfa.*

## CONDENSED STATISTICS.

No. of Experiment.	Kilos. of Sand.	Nitrogen Supplied.				Soil Infusions	Water added during Growth.	Root Tubercles at Harvest.	Mature Plants.					Nitrogen at End of Experiment.			Gain of Nitrogen.	
		In Seed. <sup>1</sup>	In Nutritive Solutions.		Total.				Number.	Branches.	Height.	Weight.			In Plant.	In Nutritive Solutions.		Total.
			1888.	1889.								Tops.	Roots (and Sand).	Total.				
109	12	Mg. ..	Mg. ...	Mg. ...	Cc. 50	Cc. 8700	Fair number.	3	16	Inches. 12-20	G. 3.22	G. 7.76	G. 10.98	Mg. 137.5	Mg. ...	Mg. 137.5	Mg. 137.5	
111	12	..	113	227.6	..	8900	Few.	1	14	18	5.13	5.83	10.96	223.0	121.9	344.9	4.3	
112	12	..	113	227.6	..	11100	Few.	1	13	28	10.27	10.12	20.39	440.0	109.8	549.8	209.2	
113	12	..	113	227.6	50	12700	Large number.	1	35	20	12.90	18.45	31.35	648.4	74.3	722.8	382.2	
114	12	..	113	227.6	50	9400	Few.	3	20	10-20	5.63	7.97	13.60	251.0	128.0	379.0	38.4	

<sup>1</sup> The weights of the seeds and nitrogen supplied in them were very small and are omitted.

EXPLANATION OF TABLE.—In July, 1883, a number of experiments with alfalfa were started. The plants developed very slowly, and at the approach of cold weather were housed for the winter, during which season they made practically no growth. In the spring of 1889, the sand in each pot in which the plants had survived was extracted with water, the nitrogen (in nitrates) determined, and the difference between the amount of nitrogen thus found and that originally supplied in the nutritive solutions charged to the plants. The plants were transplanted into pots containing freshly purified sand and allowed to grow during the spring and summer. In pots Nos. 111-113 two plants each died. The nitrogen in the plants which died was not estimated, hence whatever nitrogen they may have taken from the nitrates supplied is counted as equivalent to so much lost. Only five experiments were carried to a successful completion, one without and four with the addition of nitrogen as nitrates. The plants of three of these experiments, Nos. 109, 113 and 114, were each treated with 25 cc. of an infusion of soil in which alfalfa had been growing luxuriantly and 25 cc. of pea-soil infusion.

TABLE V.—Series XII, 1889. *Oats.*

## CONDENSED STATISTICS.

No. of Experiment.	Nitrogen Supplied.			Soil Infusions.	Water added during Growth. <sup>1</sup>	Duration of Growth. <sup>1</sup>	Root Tubercles at Harvest.	Mature Plants.						Nitrogen at End of Experiment.			Gain (or Loss) of Nitrogen.
	Kilos. of Sand.	In Seed.	In Nutritive Solutions.					Total.	Weight.				In Plants.	In Nutritive Solutions.	Total.		
									Vines and Fruit.	Roots (and Sand).	Total.	No. of Vats.				Height.	
		Mg.	Mg.	Mg.	Cc.	Days			Ft.	G.	G.	G.	Mg.	Mg.	Mg.		
167	6	4.1	...	4.1	4100	84	None on any of the Plants.	6	7	.75	.56	9.70	19.64	177.5	19.7	197.2	-111.5
168	6	4.2	...	4.2	4100	84		6	7	.68	.58	4.96	16.25	205.5	8.1	213.6	-94.2
169	6	4.3	...	4.3	4300	84		6	8	.72	.62	7.60	19.20	197.1	11.8	208.9	-98.9
170	6	3.8	...	3.8	4100	84		6	6	.69	.56	10.50	19.00	160.9 <sup>2</sup>	9.1	170.0 <sup>2</sup>	...
171	6	4.2	303.5	307.7	...	84		6	3	9.94	9.70	6.10	21.90	391.7	25.7	417.4	-194.0
172	6	4.3	303.5	307.8	...	84		6	3	11.29	4.96	10.60	24.68	396.8	40.2	437.0	-174.4
173	6	4.3	303.5	307.8	50	84		6	3	11.60	7.60	8.50	19.00	160.9 <sup>2</sup>	9.1	170.0 <sup>2</sup>	...
174	6	4.3	303.5	307.8	50	84		6	3	10.50	8.50	6.10	21.90	391.7	25.7	417.4	-194.0
175	6	4.3	607.0	611.4	...	84		6	3	15.80	6.10	10.60	24.68	396.8	40.2	437.0	-174.4
177	6	4.3	607.0	611.4	50	84		6	3	14.08	10.60	24.68	396.8	40.2	437.0	-174.4	-255.1
178	6	4.1	607.0	611.1	50	84		6	3	13.62	10.19	23.81	332.2	23.8	356.0	-255.1	-255.1

<sup>1</sup> The plants in Nos. 167-170 had finished their growth, but the others were a little past the "milk" when harvested.

<sup>2</sup> In the determination of nitrogen in plants a portion (estimated at one-fifth) was lost. The results were sufficient to indicate that there had been considerable loss of nitrogen in the experiment and to imply that the actual quantity of nitrogen in the plants was about the same as that of the others (Nos. 171-173) of this group.

EXPLANATION OF TABLE.—In Experiments Nos. 167-170, no nitrogen was added other than that contained in the seeds. Nos. 171-174 received a small proportion and Nos. 175-178 a larger proportion of nitrogen as nitrates. In each of six cases 50 cc. of pea-soil infusion were added.



TABLE VI.—*Series IX, 1888. Corn.*

CONDENSED STATISTICS.

No. of Experiment.	Kilos. of Sand.	Weight of Seed.	Nitrogen Supplied.			Soil Infusions.	Water added during Growth.	Root Tubercles at Harvest.	Mature Plants.				Nitrogen at End of Experiment.			Gain (or Loss) of Nitrogen.	
			In Seed.	In Nutritive Solutions.	Total.				Number.	Weight.			In Plant.	In Nutritive Solutions.	Total.		
										Tops.	Roots (and Sand).	Total.					
48	9	929.5	Mg. 17.9	Mg. ...	Mg. 17.9	Cc. ...	5900	None on any of the Plants.	2	G. 2.132	G. 5.287	G. 7.419	Mg. 21.6	..	Mg. 21.6	Mg. 3.7	
49	9	941.7	18.1	..	18.1	..	5900		1	.176	1.478	1.654	6.7	..	..	6.7	-11.4
25	16	942.0	18.1	..	18.1	25	11300		2	5.093	8.028	13.121	38.1	..	..	38.1	20.0
36	16	969.9	18.6	..	18.6	25	10900		2	4.272	11.050	15.322	38.7	..	..	38.7	20.1
26	16	979.5	18.8	113.8	132.6	..	12700		2	21.490	26.800	48.290	170.5	..	..	170.5	37.9
27	16	966.2	18.6	113.8	132.4	..	12200	2	23.960	27.890	51.850	154.5	..	..	154.5	22.1	
34	15	975.9	18.7	113.8	132.5	25	11800	2	21.730	16.220	37.950	135.6	..	..	135.6	3.1	
35	15	974.1	18.7	113.8	132.5	25	12100	2	21.260	18.790	40.050	130.8	..	..	130.8	-1.7	

EXPLANATION OF TABLE.—In the first four experiments no nitrogen was added; in the last four experiments a small proportion was added in the form of nitrates. In one-half the cases 25 cc. of an infusion from the soil in which corn was growing were added in each case. In all of the experiments the quantity of food supplied to the plants was insufficient for the normal growth.

TABLE VII.—Series XIII, 1889. *Corn.*

CONDENSED STATISTICS.

No. of Experiment.	Kilos. of Sand.	Weight of Seed.	Nitrogen Supplied.			Soil Infusions.	Water added during Growth.	Duration of Growth.	Root Tubercles at Harvest.	Mature Plants.										Nitrogen at End of Experiment.			Gain (or Loss—) of Nitrogen.
			In Seed.	In Nutritive Solutions.	Total.					Height.		Weight.		In Plants.	In Nutritive Solutions.	Total.							
										Inches.	Greatest.	Tops.	Roots (and Sand).				Total.	Mg.	Mg.	Mg.			
		Mg.	Mg.	Mg.	Cc.	Cc.	Days.			Number.	Inches.	Inches.	G.	G.	G.	Mg.	Mg.	Mg.					
179	9	1150	21.1	...	21.1	4800	106	None on any of the Plants.		2	10,	8	20,	23	3.60	5.55	9.15	31.2	...	31.2	10.1		
180	12	1114	20.4	...	20.4	5000	107			2	5,	9	18,	28	4.85	4.60	9.45	35.8	...	35.8	15.4		
181	12	1183	21.6	...	21.6	5000	107			2	7,	8	16,	24	3.55	3.35	6.90	27.6	...	27.6	6.0		
182	12	1186	21.7	...	21.7	5000	107			2	7,	8	22,	22	3.60	3.35	7.40	31.5	...	31.5	9.8		
183	12	1114	20.4	...	20.4	4900	106			2	8,	8	24,	28	4.20	3.15	7.35	32.7	...	32.7	10.3		
184	12	1106	20.3	...	20.3	4900	106			2	10,	6	25,	22	2.85	2.60	5.45	25.8	...	25.8	5.5		
185	11	578	11.6	417.3	428.9	8700	127			1	45	56	22.85	13.42	22.85	13.42	36.27	323.9	...	323.9	-105.0		
186	16	1081	19.8	607.0	626.8	13500	127			2	57,	34	57,	43	48.85	12.27	61.12	509.1	4.1	513.3	-113.5		
187	17	1098	20.1	607.0	627.1	13200	127			2	52,	57	52,	60	42.33	15.88	58.21	486.9	...	486.9	-140.2		
188	17	1146	21.0	607.0	628.0	12600	127			2	52,	50	52,	60	51.72	17.51	69.23	535.3	...	535.3	-92.7		
189	17	1126	20.7	607.0	627.7	13700	127	2	54,	49	54,	49	54.90	14.80	69.70	534.0	14.9	544.9	-78.8				
190	17	1159	21.2	607.0	628.2	14100	127	2	46,	26	52,	43	50.07	18.93	69.00	569.9	...	569.9	-58.3				
191	22	1111	20.4	1631.4	1651.8	16900	127	2	60,	71	94.00	20.35	114.35	20.35	114.35	1213.7	106.8	1320.5	-331.3				
192	22	1174	21.5	1517.6	1539.1	16600	127	2	58,	63	58,	63	78.42	21.35	99.77	1185.2	79.9	1265.1	-274.0				
193	29	1179	21.6	1517.6	1539.2	21900	127	2	64,	66	64,	66	89.03	34.82	123.85	1340.7	4.8	1345.5	-193.7				
194	22	1138	20.8	1517.6	1538.4	18400	127	2	61,	49	61,	59	74.33	21.80	96.13	1300.8	10.4	1311.2	-227.2				
195	22	1081	18.5	1517.6	1536.1	18300	127	2	66,	50	60,	50	67.04	29.14	96.18	1367.2	...	1367.2	-168.0				
196	30	1114	20.4	1517.6	1538.0	21900	127	2	46,	58	46,	58	75.30	37.85	113.15	1312.3	...	1312.3	-225.7				

EXPLANATION OF TABLE.—In Nos. 179-184 no nitrates were supplied; in Nos. 185-190 a small proportion; and in Nos. 191-196 a large proportion of nitrogen was added in the form of nitrates. To one-half of the experiments of each group 50 cc. of an infusion of a soil in which corn was growing were added. Under "Height," the length of the plant from soil to top of tassel is stated as height of stem; the greatest height was found by measuring from the soil to the extremity of the longest leaf. Analyses of the residual solutions, from time to time, implied that none of the plants had received enough food for normal growth.

ANALYTICAL DETAILS.

Determinations of nitrogen were made in seeds, nutritive solutions, residual solutions, and plants, by the method described under "Methods of Analysis" above. The details of the determinations of nitrogen in the plants are omitted here for the reason there given. The details of determinations of nitrogen in seeds, nutritive solutions and residual solutions follow.

*Nitrogen in Seed. Method of Kjeldahl.*

No. of Series.	Kind of Seed.	Weight of portion taken for analysis.	Nitrogen Found.		
			Weight.	Percentage.	Average percentage
VII.	Champion of England Peas,	Mg.	Mg.		
		1001.0	43.75	4.37	4.39
		1001.3	44.42	4.42	
		1002.0	43.96	4.39 <sup>1</sup>	
IX.	Corn, . . . . .	1001.0	18.98	1.90	1.92
		1000.5	18.91	1.89	
		1002.0	19.27	1.92	
		1003.5	19.60	1.95	
X.	East Hartford Early Peas,	1000.	39.90	3.99	4.01
		1000.	40.19	4.02	
		1000.	40.19	4.02	
XI.	Champion of England Peas,	1000.	45.62	4.56	4.57
		1000.	45.80	4.58	
		1000.	45.80	4.58	
XII.	Oats, . . . . .	1000.	19.13	1.91	1.88
		1000.	18.60	1.86	
		1000.	18.70	1.87	
XIII.	Corn, . . . . .	1000.	18.50	1.85	1.83
		1000.	18.20	1.82	
		1000.	18.20	1.82	

<sup>1</sup>Soda-lime method.

*Nitrogen in "N. III" Solution, 1888.*

25 cc. from "N. III" pipette  $\left\{ \begin{array}{l} 37.69 \text{ mg. N.} \\ 37.64 \text{ " " } \\ 37.64 \text{ " " } \end{array} \right\}$  Average 37.66 mg. N.

*Nitrogen in "N. III" Solution, 1889.*

25 cc. from "N. III" pipette  $\left\{ \begin{array}{l} 37.93 \text{ mg. N.} \\ 37.87 \text{ " " } \\ 38.03 \text{ " " } \end{array} \right\}$  Average 37.94 mg. N.

*Nitrogen in Residual Solutions.*

Series No.	Experiment No.	Liters of Extract.	Nitrogen found in one liter of Extract.			Total Nitrogen in residual solution.
			A.	B.	C.	
IX.	158	3	0.62	0.63		1.9
	159	3	0.68	0.65		2.0
	161	3	0.69	0.66		2.0
	163	4	0.57	0.63		2.4
	164	3	5.65	5.48	5.37	17.5
	165	4	5.87	5.87		23.5
	166	5	21.58	20.61		105.5
VII.	86	3	8.35	8.20		24.8
	87	3	8.41	8.68		25.6
	88	3	8.10	7.88	8.23	24.2
	89	3	19.09	19.00		57.2
	91	3	21.16	21.47	21.54	64.0
	92	3	23.21	23.09		69.4
	93	3	5.58	5.76	5.68	17.0
	94	3	9.55	9.30		28.2
	95	3	12.68	12.75		38.1
	96	3	31.69	31.65		95.0
	103	3	8.30	8.70	8.45	25.5
	104	3	0.73	0.76		2.2
	105	3	4.97	5.17		15.4
	107	3	2.91	2.88		8.6
X.	129	3	2.53	2.68	2.60	7.8
	130	3 <sup>1</sup>	0.58	0.58		1.7
	130	3	5.58	5.61	5.81	17.0
	131	3	0.68	0.60		1.9
	132	3	2.80	2.75		4.7
	133	3	0.51	0.62		1.7
	141	3	0.70	0.70		2.1
	143	4	0.89	0.94		3.7
	144	4	0.71	0.63	0.58	2.5
	146	4	1.15	1.15		4.6
	147	4	6.70	6.50		26.4
	149	3	0.57	0.51		1.6
	150	3	10.96	10.96		32.9
XI.	111	5 <sup>2</sup>	18.94	18.97		105.4
	111	5	3.29	3.31		16.5
	112	5	14.73	14.73		79.2
	112	5	2.34	2.35		11.8
	112	3 <sup>1</sup>	6.29	6.29		18.8
	113	5 <sup>2</sup>	4.59	4.57		27.9
	113	3 <sup>1</sup>	12.85	12.85		38.5
	113	5	1.57	1.50	1.66	7.9
	114	5 <sup>2</sup>	16.57	16.74		83.3
	114	5	7.24	7.04	{ 6.64 } { 6.84 }	34.7

<sup>1</sup> In residual solutions.<sup>2</sup> In solutions of 1888.

*Nitrogen in Residual Solutions.—Continued.*

Series No.	Experiment No.	Liters of Extract.	Nitrogen found in one liter of Extract.			Total Nitrogen in residual solution.
			A.	B.	C.	
XII.	171	4	4.39	4.46		17.7
	171	3 <sup>1</sup>	0.65	0.68		2.0
	172	4	2.01	2.01		8.1
	173	4	2.97	2.95		11.8
	174	4	2.27	2.27		9.1
	175	4	6.46	6.38		25.7
	177	4	10.11	10.01		40.2
	178	4	9.27	9.17		36.9
XIII.	186	6	0.69	0.72		4.1
	189	6	0.57	0.55		3.4
	191	5 <sup>1</sup>	21.36	21.38		106.9
	192	5	15.96	15.97		79.9
	193	6	0.80	0.79		4.8
	194	6	1.73	1.73		10.4

In the following cases, either no nitrogen was supplied in the nutritive solutions, or the residual solutions contained no nitrogen :

Series XI, Nos. 151-157, 160 and 162.

Series VII, Nos. 81-84, 97-102, 106 and 108.

Series X, Nos. 115-128, 134-140, and 145.

Series VIII, No. 109.

Series IX, Nos. 25-27, 34-36, 48-49.

Series XII, Nos. 167-170.

Series XIII, Nos. 179-185, 187, 188, 190, 195 and 196.

## REVIEWS AND REPORTS.

### SYNTHETICAL EXPERIMENTS IN THE SUGAR SERIES.

An interesting address<sup>1</sup> upon the synthesis of the sugars was given by Professor Emil Fischer at a meeting of the Berlin Chemical Society, held on June 23, 1890. On this occasion a number of new sugars and their derivatives were described for

<sup>1</sup> Ber. d. chem. Ges. **23**, 2114.

the first time. Of especial interest is the announcement of the discovery of the optical isomers of dextrose and levulose and of gluconic and saccharic acids. So that to-day, as a result of his work, it is not only possible to prepare the natural sugars dextrose and levulose by synthetical methods, but also the optical isomers of these sugars as well. When these experiments were begun in 1887, only four sugars of the formula  $C_6H_{12}O_6$  were known, namely, dextrose, levulose, galactose, and sorbinose. Now we have no less than fourteen such compounds, and all but two of them have been made synthetically. Furthermore, the existence of all these new sugars is in accordance with the deductions of the Le Bel-van't Hoff hypothesis.

Looking at Professor Fischer's work as a whole, it is worthy of note that, apart from the splendid achievement of effecting the synthesis of grape sugar and fruit sugar, he has discovered and developed several new and important reactions which are of wide application in organic chemistry. His success depends in no small degree upon the use which he has made of these reactions. Among the most important of these are undoubtedly the phenylhydrazine reactions. The hydrazones and osazones are the compounds formed by the action of phenylhydrazine upon the sugars and the compounds analogous with them. The methods for preparing these substances, as well as the more important transformations which they undergo, have already been described in previous reports<sup>1</sup> in this Journal. On account of the readiness with which they crystallise and the ease with which they can be obtained in pure condition they are invaluable for the purpose of detecting and purifying the sugars. The osazones, further, by treatment with hydrochloric acid are converted into osones, and these substances by reduction are transformed into ketone sugars. It is, therefore, possible in this way to change all aldehyde sugars, of which grape sugar may be taken as an example, into the corresponding ketone sugars, of which fruit sugar is a good representative. The osazones, too, are of value for determining the composition and constitution of the several sugars. The carbohydrates  $C_5H_{10}O_5$ ,  $C_6H_{12}O_6$ ,  $C_7H_{14}O_7$ , etc., all have the same percentage composition; an analysis alone, therefore, would not be sufficient for determining the molecular formula of any one of them. This result could be attained by analysing the osazone, and, moreover, the osazone possesses the advantage of being a derivative that can be easily prepared in pure condition. The hydrazones and osazones are, however, especially valuable for the isolation of new sugars, and compounds analogous to the sugars. Phenylhydrazine also unites with the acids of the sugar series and forms compounds called hydrazides. These substances have proved to be of value in separating and purifying the sugar-acids.

<sup>1</sup> This Journal 11, 277; 12, 357.



Another reaction of no less importance is the reduction of the lactones of the sugar-acids with nascent hydrogen. This reaction, together with the well known methods for preparing acids, make it possible to build up whole series of sugars from simpler ones containing a small number of carbon atoms. The sugars, like other aldehydes and ketones, unite directly with hydrocyanic acid, and the cyanhydrines which are thus formed can be readily transformed into acids containing one carbon atom more than the original sugar. Now by means of the reaction just mentioned it is possible to convert these acids into the corresponding sugars. Thus, for example, arabinose,  $C_5H_{10}O_5$ , unites with hydrocyanic acid and forms the cyanhydrine  $C_6H_{11}O_5.CN$ . This compound when boiled with alkalis is converted into arabinosecarbonic acid,  $C_5H_{11}O_5.CO_2H$ ; and the lactone of the latter substance when reduced with sodium amalgam is transformed into *l*-mannose,  $C_6H_{12}O_6$ . Then the process of lengthening the chain of carbon atoms can be repeated and a sugar of the formula  $C_7H_{14}O_7$  obtained. Dr. Fischer has prepared in this way from arabinose new sugars with six, seven, eight, and even nine carbon atoms. There is no reason—except perhaps lack of material—why the process should not be carried still farther.

The preparation of so many new sugars by this method has necessitated the adoption of a new nomenclature for these compounds. It is suggested<sup>1</sup> that a sugar be named according to the number of carbon atoms which it contains, as a triose, tetrose, pentose, hexose, heptose, octose, nonose, etc. Further, each individual isomer of the same series is to be distinguished by adding a prefix to the name which shall indicate its derivation. For example, "mannoheptose" means a sugar with seven carbon atoms,  $C_7H_{14}O_7$ , prepared from mannose. The names dextrose and levulose are to be dropped entirely, and instead of the former it is suggested that the name *glucose*, and for the latter *fructose* be substituted. The optical isomers are designated by means of the letters *d*, *l* and *i*, placed before the names of the sugars. The general name for a sugar containing the aldehyde group is *aldose*, and for a ketone sugar *ketose*.

The advantages of the new system of nomenclature can best be seen in the following table which contains the names of all the simple sugars known at the present time:

Triose: Glycerose. (Mixture of glyceric aldehyde and dioxycetone.)

Tetrose: Erythrose. (Probably a mixture of aldose and ketose.)

Pentoses: Arabinose. (Aldose.)

Xylose.

Methylpentose, or Rhamnose. (Aldose.)

<sup>1</sup> Ber. d. chem. Ges. 23, 2136.

Hexoses:	<i>d</i> -, <i>l</i> -, <i>i</i> -Glucose,	} Aldose sugars, } Mannite series.
	<i>d</i> -, <i>l</i> -, <i>i</i> -Mannose,	
	<i>d</i> -, <i>l</i> -, <i>i</i> -Fructose. (Ketose.)	
	Galactose. (Aldose of the dulcite series.)	
	Sorbinose.	
	Formose,	} Constitution unknown.
	$\beta$ -Acrose,	
	Methylhexose, Rhamnohexose. (Aldose.)	
Heptoses:	Mannoheptose,	} Aldose sugars.
	Glucoheptose,	
	Galaheptose,	
	Fructoheptose,	
	Methylheptose, Rhamnoheptose,	
Octoses:	Mannoctose,	}
	Glucocotose,	
	Rhamnooctose,	
Nonnose:	Mannononose,	}

Glycerose and erythrose are obtained by the oxidation of glycerine and erythrite respectively. Arabinose is an aldehyde sugar with a normal chain of carbon atoms, and can be easily transformed into *l*-mannose. The constitution of xylose has not yet been determined. Rhamnose is also classified with the pentoses because it may be regarded as a methyl derivative of arabinose. Under the hexoses grape sugar is classified as *d*-glucose and fruit sugar as *d*-fructose. The optical isomers of these sugars, lately discovered, are *i*- and *l*-glucose and *i*- and *l*-fructose. Methylhexose has been prepared synthetically from rhamnose by the reactions described above. The higher sugars in the list have also been prepared by this synthetical method, and their origin is designated by the prefixes manno-, gluco-, gala-, and fructo-. Most of these new compounds surpass the derivatives of the natural hexoses in power of crystallisation. The most interesting among them is mannononose, because with yeast it ferments as easily as glucose. The octoses, heptoses and pentoses cannot be fermented, but glycerose and most of the hexoses possess this property.

Many of these new sugars will probably be found to occur in nature. Already the new sugar mannose has been found in a number of plants, and has been obtained in quantity from the reserve cellulose of vegetable ivory. There are indications that others also occur in the vegetable world. Thus mannoheptose by reduction is converted into a heptacid alcohol  $C_7H_{16}O_7^1$ , and this compound has been found to be identical with Perseite,<sup>2</sup> a compound which occurs in the fruit of *Laurus Persea*.

To show just how these new reactions were of service in effecting the synthesis of the sugars, it may, perhaps, be of interest to

<sup>1</sup> Ber. d. chem. Ges. 23, 2231.

<sup>2</sup> Ann. chim. phys. [6] 19, 5; This Journal 12, 284.

recall briefly the different steps in Prof. Fischer's investigation. He began his work by studying the oxidation of polyacid alcohols, such as glycerine, erythrite, and mannite. It had long been known that compounds analogous to the sugars are formed by the oxidation of these substances, but the greatest difficulty was experienced in attempting to separate these compounds from the other oxidation products. Here the phenylhydrazine reaction proved to be of great value. Glycerose and erythrose were separated in the form of beautifully crystallised osazones, the former from the oxidation products of glycerine, the latter from those of erythrite. Mannite by oxidation gave fruit sugar and a new sugar called *d*-mannose, the latter being discovered by means of its hydrazone. Mannose on investigation was found to be an aldehyde sugar of the same constitution as grape sugar, and proved to be a stereometric isomer of the latter substance. It was also found that *d*-mannonic acid by heating with quinoline could be changed into gluconic acid, and the latter compound when reduced with sodium amalgam was transformed into grape sugar. *d*-Mannose was also easily converted into fruit sugar, for on treating it with phenylhydrazine the same osazone is obtained as from grape sugar and fruit sugar, namely, glucosazone. Glucosazone by treatment with concentrated hydrochloric acid is converted into glucosone, and the latter compound by reduction is transformed into fruit sugar. It is evident, therefore, that if *d*-mannose or *d*-mannonic acid be prepared synthetically, the synthesis of dextrose and levulose is also accomplished.

The condensation of formic aldehyde and of glycerose and the action of alkalis upon acrolein bromide give rise to the formation of substances resembling the sugars. Professor Fischer and his co-workers succeeded in obtaining from these substances a sugar having the formula  $C_6H_{12}O_6$ , and which is known as *α*-acrose. The osazone of this sugar is identical with glucosazone, except that it is optically inactive. By reduction the new sugar is converted into a hexacid alcohol called *α*-acrite, which has all the properties of mannite but that of turning the ray of polarised light. In short *α*-acrite is *z*-mannite.

The next step would naturally have been to separate the *α*-acrite, or one of its derivatives, into the optically active components. In this way *d*- and *l*-mannite would have been obtained, and the former by easy transformations could have been converted into *d*-mannose, and this into fruit sugar; further, by oxidation the *d*-mannose could have been changed into *d*-mannonic acid, and then the latter compound could have been converted into grape sugar. These changes unfortunately could not be carried out with the *α*-acrite obtained by synthesis, because of lack of material. Owing to the many transformations involved in making *α*-acrite, and the very small yield obtained in some of the reactions, a kilogram of glycerine gave only 0.2 gram *α*-acrite.

The complete synthesis of the sugars would probably not have been effected so soon had not Dr. Fischer at this stage of the work made the fortunate discovery that arabinosecarbonic acid and *d*-mannonic acids are optical isomers, and that these acids combine to form an optically inactive compound of the same composition. By means of the new reaction for reducing sugar acids, this inactive acid, *i*-mannonic acid, was converted into *i*-mannose, and the latter by further reduction into *i*-mannite. But *i*-mannite and *α*-acrite are identical substances, and thus a new starting point for the synthesis of the natural sugars was obtained. *α*-Acrite, or *i*-mannite, and its derivatives, could now be prepared in quantity from arabinose and *d*-mannose, two sugars that occur in nature. It only remained to split into optically active isomers<sup>1</sup> *i*-mannite or one of its derivatives. The derivative selected for this purpose was *i*-mannonic acid, and this by means of its strychnine and morphine salts was biparted and *d*- and *l*-mannonic acids obtained. These bipartites by reductions were converted into *d*- and *l*-mannose, and thus all the steps in the synthesis of the sugars had been taken, for, as stated above, *d*-mannose can be transformed into fruit sugar, and *d*-mannonic acid into gluconic acid and grape sugar.

The table below (see next page) contains all the compounds belonging to the mannite group of sugars known at present, and also shows the relations which they bear to one another.

*l*-Gluconic acid and *l*-glucose and *l*-saccharic acids are obtained from *l*-mannonic acid in the same way that the corresponding *d*-derivatives are prepared from *d*-mannonic acids. As was to be expected, these compounds resemble very closely the well known compounds of the *d* series, and each one unites with its optical isomer to form an inactive compound. In this way the three compounds *i*-gluconic acid, *i*-saccharic acid and *i*-glucose are obtained. It was also observed that *l*-gluconic acid can be obtained in abundant quantity from the mother-liquors obtained in the preparation of *l*-mannonic acid from arabinose. *l*-Glucose, like *l*-mannose and *l*-fructose, cannot be fermented with yeast, but in all other respects it is very similar to its optical isomer, except, of course, that it rotates the polarised ray as much to the left as *d*-glucose does to the right.

Omitting the compounds containing nitrogen, there are now 26 substances known that belong to the mannite series, and no compound has thus far been discovered which in any way contradicts the deductions of the Le Bel-van't Hoff hypothesis. Nevertheless, the exact relation which *d*-mannonic acid and *d*-gluconic acid

<sup>1</sup>As there is no word in the English language for describing this kind of chemical change, it might, perhaps, be well to adopt for this purpose the following terms:

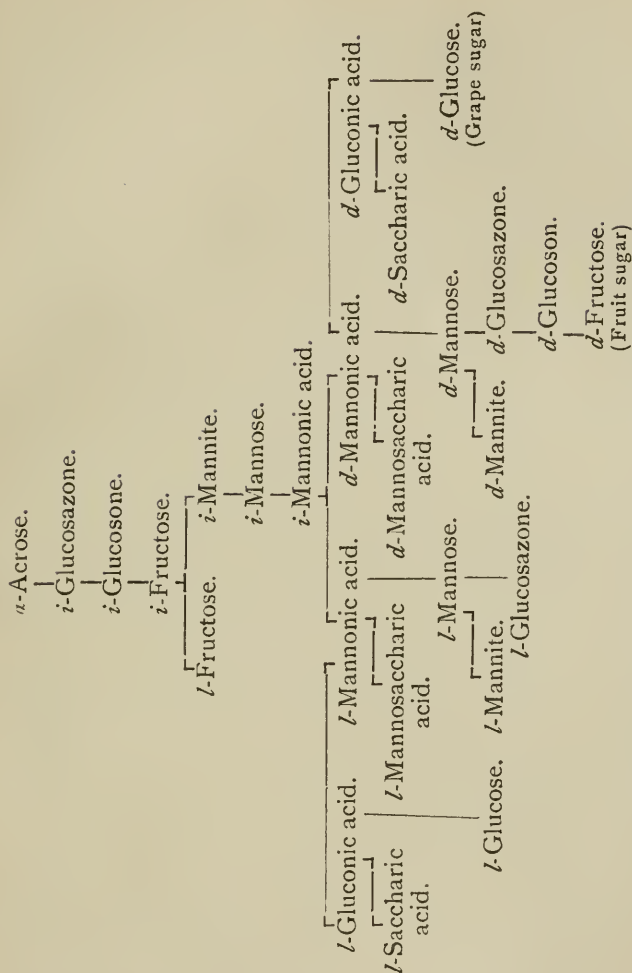
Bipart, to separate a compound into its optically active isomers (*dedoubler* in French).

Bipartition, the act of separating a compound into optically active isomers.

Bipartient, that which causes bipartition.

Bipartile, a compound that can undergo bipartition.

Bipartite, a compound obtained by bipartition.—E. H. K.



bear to each other is not yet quite clear. In general, the results of this investigation tend to confirm the principle that for every optically active compound there is an optical isomer which can unite with it to form an inactive substance. But gluconic and mannonic acids cannot be made to unite with one another to form an inactive compound, although they can be changed one into the other by heating with quinoline.

Some interesting problems for investigation suggest themselves. Grape sugar and fruit sugar appear to be the first products of



assimilation in plants; now, does the synthesis of these compounds throw any light upon their formation in nature? As yet, almost nothing is known with certainty about the method of formation of the carbohydrates in green leaves. v. Baeyer has suggested the idea that carbonic acid is first reduced to formic aldehyde, and then by condensation the latter substance is converted into sugar. But as yet no one has succeeded in obtaining evidence of the presence of at all appreciable quantities of formic aldehyde in green leaves, and, perhaps, in future investigations upon this subject better results would be obtained if the attempt were made to detect glycerose or other intermediate products by means of the new methods. Another question in physiological chemistry suggests itself. Why are only the optically active sugars of the *d*-mannite series found in nature? Are they the only products of assimilation, and is the formation of optically active substances a prerogative of living organisms, brought about by a special cause, a kind of vital force? Prof. Fischer is inclined to think that this is not the case, but that in all probability inactive substances are first formed in the plant and that these then undergo bipartition, and the sugars of the *d*-mannite series are used in the formation of starch, cellulose, inuline, etc., while the optical isomers are used for other purposes that are as yet unknown to us.

What will be the effect of the new sugars, such as mannnonose and the pentoses and heptoses, upon animal bodies? What changes will these new sugars cause in the blood and tissues of animals if used as food? These are interesting problems for the physiological chemist to solve. The assimilating plant prepares from sugar not only the most complicated carbohydrates and fats, but also with the addition of nitrogenous inorganic compounds it forms proteïds. Moulds and bacteria also have this power. Now, if it should be possible to nourish the plant or the bacteria with a sugar of different composition, it might be possible to obtain in this way a new kind of albumen. And with a change in the building material, may we not expect a change in the architecture? Prof. Fischer thinks that in this way it might be possible to exert a chemical influence upon organisms which would cause the most remarkable phenomena, changes of form which would far surpass anything that has hitherto been attained by breeding and intercrossing.

E. H. KEISER.

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#### THE ACTION OF CARBON MONOXIDE ON NICKEL.

Under the above title L. Mond, C. Langer and F. Quinke have recently<sup>1</sup> made known the results of their investigations upon the action of carbon monoxide upon heated metals, and upon nickel in particular.

<sup>1</sup>J. Chem. Soc. 57, 749.



"When carbon monoxide is passed over finely-divided metallic nickel at a temperature between  $350^{\circ}$  and  $450^{\circ}$ , carbon dioxide is formed, and a black amorphous powder is obtained consisting of nickel and carbon. The composition of this powder varies very widely with the temperature employed, and still more according to the time the operation has been carried on. A small amount of nickel can decompose a very large amount of carbon monoxide."

"The carbon contained in this substance is very readily attacked by steam; at the comparatively low temperature of  $350^{\circ}$  hydrogen and carbon dioxide are obtained without a trace of carbon monoxide." When the compound was heated and then allowed to cool in a current of carbon monoxide it was found that a volatile compound of nickel was obtained, for on passing the gases through a heated tube a mirror of metallic nickel was deposited on the walls of the tube. It was then found that on heating finely-divided metallic nickel to about  $400^{\circ}$  and afterwards allowing it to cool in a slow current of carbon monoxide, the gas is readily absorbed, and of the mixture of gases given off, as much as 30 per cent., in some cases, may be condensed by means of a suitable cooling apparatus and obtained in the form of a clear, volatile liquid. If the vapor of this liquid be passed through a tube heated above  $150^{\circ}$  it is decomposed with the deposition of metallic nickel, usually contaminated with carbon resulting from the action of metallic nickel upon free carbon monoxide. It was found, however, that at  $180^{\circ}$  the deposit consisted of pure nickel, and advantage was taken of this fact to make analyses of the liquid. It was found to consist of nickel and carbon monoxide in the proportions represented by the formula  $\text{Ni}(\text{CO})_4$ .

The vapor of "nickel-carbon-oxide," when mixed with other gases, is not affected by alkalis or acids, but it reduces a solution of copper chloride in ammonia, finally precipitating the copper as such. It also precipitates silver from ammoniacal solutions of the chloride. It is decomposed by chlorine and bromine. The electric spark slowly breaks it up into nickel and carbon monoxide. The liquid nickel-carbon-oxide is mobile, highly refractive; boils at  $43^{\circ}$ , solidifies at  $-25^{\circ}$ ; its specific gravity is 1.3185 at  $17^{\circ}$ . It is unaffected by dilute acids or alkalis or by strong hydrochloric acid. The vapor density corresponds with the formula  $\text{Ni}(\text{CO})_4$ . Determinations of the atomic weight of nickel were made, the pure metal deposited in a heated tube being employed. The average of three results is 58.58. Numerous attempts to form similar compounds of other metals met with no success.

WYATT W. RANDALL.

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#### THE INFLUENCE OF "NEUTRAL" SOLVENTS.

Although it has frequently been observed that the velocity of chemical action is influenced by so-called neutral solvents, only

very recently has any attempt been made systematically to study this influence. Now, however, Menshutkin, who has distinguished himself in allied fields of investigation, has taken up this subject and has determined the velocity of combination of triethylamine and ethyl iodide in twenty-three solvents.<sup>1</sup> His results are as follows:

1. The reaction is slowest in hydrocarbons and simple ethers; and then come the esters, the alcohols and, finally, the ketones. If we represent the coefficient of velocity in the case of hexane as 1, it is 4.2 with ethyl ether, 123.9 with ethyl acetate, 203.3 with ethyl alcohol and 337.7 with acetone.

2. When homologues are used as menstrua the velocity is greatest with that having the smallest molecular weight, and *vice versa*. With methyl alcohol it is 286.6, and with ethyl alcohol 203.3; with anisol it is 223.9, and with phenetol 117.7 (hexane = 1).

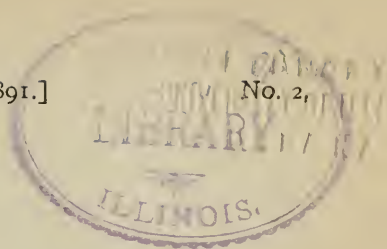
3. When two menstrua resemble each other otherwise, the velocity is greater with that having a "double bond." The benzene condition seems to favor high velocities, and so does, even more markedly, the naphthalene condition.  $k$  is equal to 203.3 with ethyl alcohol, and 240.5 with allyl alcohol. It is equal to 150 with brombenzene, and 627 with  $\alpha$ -bromnaphthalene.

4. Chlorine derivatives give greater values for  $k$  than the hydrocarbons themselves, and smaller values than bromine derivatives. The value of  $k$  with benzene being 38.2, it is 128 with chlorbenzene, and 150 with brombenzene.

These results show that the influence of solvents on the velocity of chemical action depends upon their chemical and not upon their physical properties, and that similar effects are produced by similar changes in the menstrua and in the reagents. An illustration will make this clear. The velocity is greater if methyl alcohol is used as a solvent than if ethyl alcohol is so employed, and it is greater with methyl iodide as a reagent than with ethyl iodide. This similarity seems to show that solution in organic solvents is not purely mechanical, but is, perhaps, as complicated as solution in water, and strengthens the view that solution is but the first phase of what in its later phases is known as chemical action.

F. LENGFELD.

<sup>1</sup> Ztschr. phys. Chem. 6, 41.



# AMERICAN CHEMICAL JOURNAL.

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Contributions from the Chemical Laboratory of Purdue University.

## IV.—CONCERNING THE PENTAGLUCOSES.

By W. E. STONE.

The two isomeric sugar-like bodies, arabinose and xylose, with the common formula  $C_5H_{10}O_5$ , corresponding in many characteristics to the true glucoses and in others quite distinct from the latter, may be referred to collectively as *pentagluco*ses. This term expresses the relation between these compounds and the true, or hexagluco<sup>s</sup>es, and has already become established by some degree of use.<sup>1</sup>

The two bodies just mentioned are the only members of this group thus far observed. Of these, arabinose has been known for more than twenty years, but was regarded until within a short time as a true glucose; while xylose is a recent discovery,<sup>2</sup> and has also been shown by Tollens and his pupils to be a pentaglucose.<sup>3</sup>

The pentagluco<sup>s</sup>es are strictly sugar-like bodies, crystallinic, sweet, reducing Fehling's solution, and dextro-rotatory. In some respects, however, they differ decidedly from the true glucoses.

<sup>1</sup> Ber. d. chem. Ges. **21**, 2151, **22**, 1046, **23**, 137, **23**, 1751; Ann. Chem. (Liebig) **249**, 227, **254**, 304; This Journal **12**, 435, etc.

E. Fischer proposes a numerical nomenclature for the different series of sugars so notably extended by his syntheses, according to which this group are called the "*pentoses*." This is perhaps preferable to the term here used, and may find adoption eventually.

<sup>2</sup> Koch; Pharm. Ztschr. f. Russland **25**, 619, etc.

<sup>3</sup> Tollens and Mayer; Ber. d. chem. Ges. **21**, 647; Tollens and Wheeler; Ann. Chem. (Liebig) **254**, 304.

They are not subject to alcoholic fermentation, as has been previously proven for arabinose,<sup>1</sup> and as I am now able to announce for xylose. As a distinctive and specific reaction, the pentaglucooses produce large quantities of furfural when subjected to the action of strong acids, and in this way are sharply separated from the true glucoses, which, under similar conditions, yield levulinic acid.<sup>2</sup> By perfected methods the amount of furfural thus obtained amounts to nearly fifty per cent., when pure arabinose or xylose is used.<sup>3</sup>

The pentaglucooses have not been observed as occurring in nature, but are obtained by hydrolysis of certain plant constituents. These mother-substances are found either normally as a part of the cellular tissues of the plant, or in some notable examples as abnormal gum-like secretions. So far as is known the substances occurring under either of the above conditions are identical, although at the present time we have no means of distinguishing between those substances which will yield arabinose from those which will yield xylose.

Arabinose has been prepared from the cellular tissues of the sugar beet,<sup>4</sup> from gum arabic,<sup>5</sup> gum tragacanth,<sup>6</sup> cherry gum,<sup>7</sup> and from wheat bran.<sup>8</sup> Xylose has been obtained from woods of different species and jute,<sup>9</sup> and from straw.<sup>10</sup> From brewers' grains, *i. e.* from the outer seed-coats of barley, both arabinose and xylose have been prepared,<sup>11</sup> while from peach gum arabinose and galactose were obtained,<sup>12</sup> and gum arabic also would seem to contain the mother-substances of arabinose and galactose.

The nature of this substance, or these substances, from which the pentaglucooses are derived is not well understood. They are of a gummy nature and may be spoken of comprehensively as *gums*, a term clearly applicable in some cases but less so in others. In normal woody tissues, for instance, it is difficult to locate any material of the nature of gums, but by means of alkalis an amorphous substance may be extracted which is insoluble in water, alcohol, and ether, and which by the action of acids may be converted into one or the other of the pentaglucooses. This substance has been variously designated as metapectic acid, arabin,

<sup>1</sup> Ann. Chem. (Liebig) **249**, 257.

<sup>2</sup> Ber. d. chem. Ges. **21**, 2150; Ann. Chem. (Liebig) **249**, 227.

<sup>3</sup> Ber. d. chem. Ges. **23**, 1751.

<sup>4</sup> Ibid. **1**, 58, 108.

<sup>5</sup> Ibid. **6**, 612.

<sup>6</sup> Sachsse u. Martin: Phytochemische Untersuchungen.

<sup>7</sup> Ibid.

<sup>8</sup> Ann. Chem. (Liebig) **249**, 239; also Ber. d. chem. Ges. **23**, 3110.

<sup>9</sup> Ann. Chem. (Liebig) **254**, 304.

<sup>10</sup> Ber. d. chem. Ges. **23**, 137.

<sup>11</sup> Ann. Chem. (Liebig) **249**, 243.

<sup>12</sup> This Journal **12**, 435.

wood gum, etc. Tollens and Allen have pointed out that the occurrence of this gummy material *in situ* corresponds closely to the lignin reaction with hydrochloric acid and phloroglucin.<sup>1</sup> Moreover, E. Schulze has lately shown that preparations of cellulose which, according to all appearances, were pure, still gave the lignin reaction and yielded an appreciable amount of furfural,<sup>2</sup> indicating that these substances are most intimately connected with the ultimate cellular tissue, from which they are separated with difficulty. Wherever these gums occur they may be recognised by the furfural reaction which characterises the pentaglucoſes. In this reaction the pentaglucoſes are doubtless formed as an intermediate product and themselves eventually yield furfural. The furfural test may therefore be applied to any crude material as a means of detecting the presence therein of these gums, which by proper treatment yield the pentaglucoſes. Indeed, the search for and ultimate preparation of arabinose and xylose from several of the materials mentioned has been based upon the results of a preliminary furfural test.

The continuation of my studies beyond this point, as described later, will perhaps increase the interest and importance attached to this group of bodies.

#### A.—Occurrence of the Pentaglucoſes.

The reliability of the furfural reaction as indicative of the presence of the pentaglucoſes, or the gums from which they are derived, having been established, and having led to the preparation of arabinose and xylose from several unexpected sources, the question naturally followed: how frequently do these bodies occur in vegetable products, or how widely diffused may they be in nature? Strictly speaking, only the gums are found under these conditions; but since they are little known except in their derivatives the pentaglucoſes, to which they seem to stand in direct relation, we may regard the former as representing the occurrence of the latter. If occurring commonly, they still find no recognition in our present analytical methods, toward which their reactions are those of the normal carbohydrates and glucoses. In the case of foods, results thus obtained may give rise to erroneous estimates of the values of certain materials, since we have no

<sup>1</sup> E. W. Allen: Inaugural Dissertation, Göttingen, 1890.

<sup>2</sup> Ber. d. chem. Ges. 23, 2579.



ground for assuming that the two classes are of equal or even similar nutritive value.

I have therefore examined a considerable variety of vegetable materials, including different parts and products of plants, for the purpose of detecting the presence of these gums as indicated by the production of furfural when treated with strong acids. The list of materials might be greatly extended, but it suffices, perhaps, to show that these bodies are much more widely and abundantly distributed than is ordinarily supposed.

The method of making these tests is practically the same as that used in the original study of the reaction. It allows of a comparison of the amounts of furfural produced from different sources under fairly constant conditions. The results, however, are not absolutely quantitative, failing to yield the highest possible amount of furfural in comparison with the method proposed by Tollens and Günther.<sup>1</sup> Having commenced these studies, however, some time since, I have preferred to retain the original method, for the sake of comparison between earlier and later results. This method is as follows:

2-5 grams of the finely powdered, air-dried material are placed in a flask of 200-300 cc. capacity, with 50 cc. of sulphuric acid of 1.254 specific gravity. The flask is placed in a paraffin bath and connected with a condenser; through a second opening in the stopper connection is made with a reservoir from which water is allowed to drop into the flask with just sufficient rapidity to replace the loss by distillation and thus maintain a constant concentration of the acid. The bath is heated to 125° to 135° C. The first action of the acid is to convert the gums into pentaglucofuranoses, followed at once by the decomposition of the latter, probably in this way,



The furfural thus formed is distilled over and collected. This distillation is continued so long as there is evidence of the presence of furfural in the distillate. This evidence is furnished by a reaction which is very delicate, and which consists in allowing a drop of the distillate to fall upon a strip of filter-paper moistened with aniline acetate. So sensitive is this reaction that one part of furfural in one hundred thousand parts of water produces instantly

<sup>1</sup> Ber. d. chem. Ges. 23, 1751.



an intense red color upon the paper. In more concentrated solutions this color becomes darker and, eventually, reddish brown.

Usually eight to ten hours are required to complete the distillation, and the distillate amounts to 200-300 cc. The furfurol contained therein is next concentrated by fractional distillation to a volume of 3-6 cubic centimeters, in which it may in part appear in the form of light-yellow oily drops. Upon the addition of dilute ammonia a precipitate of furfuralamide is formed, which is collected, dried over sulphuric acid, weighed, and the relation of its weight to that of the original material calculated in percentage. The following results therefore express the amount of *furfuralamide* obtained from the various materials. But 1 gram of furfuralamide theoretically requires for its production 1.6875 grams of a pentaglucofcs, and practically, under the conditions described, rather more. Hence the percentages given may be multiplied by the above factor (1.6875), and will then indicate *less than the actual amount* of pentaglucofcs present. From about forty substances examined, the following thirty-one yielded appreciable amounts of furfuralamide:

Hungarian grass,	3.34	per cent. of furfuralamide.
Timothy hay,	1.18	" "
Corn stover, I,	2.89	" "
" " II,	1.48	" "
Maize ensilage,	0.91	" "
Clover hay,	1.55	" "
Clover ensilage,	0.40	" "
Wheat straw,	4.16	" "
Oat straw,	2.29	" "
Malt sprouts,	1.82	" "
Brewers' grains,	7.20	" "
Corn bran, I,	0.84	" "
" " II,	1.80	" "
Linseed meal,	1.20	" "
Corn and cob meal,	0.59	" "
Corn cobs,	8.16	" "
Oatmeal,	0.40	" "
Beet pulp,	3.59	" "
Cotton-seed hulls,	3.66	" "
Pulp of strawberries,	1.95	" "
Dung of cattle fed on maize ensilage,	2.88	" "

Dung of cattle fed on corn stover,	3.94	per cent of furfuramide.
Gum arabic,	5.46	" "
Cherry gum,	8.14	" "
Gum tragacanth,	8.08	" "
Peach gum,	4.84	" "
White lupine seeds,	0.95	" "
Yellow " "	1.69	" "
Coats of orange seeds,	1.85	" "
Orange peel,	0.69	" "
Watermelon seeds,	2.70	" "

The following materials yielded no perceptible quantities of furfuramide, but all gave strong qualitative reactions for furfural, and it is hardly too much to expect that with a better method of distillation these also might yield furfural in noticeable amounts :

Dried strawberries,  
Cotton-seed cake,  
Corn meal,  
Dried sweet potato,  
Kernels of orange seeds,  
Raw coffee,  
Buckwheat,  
Beans.

Under the stated conditions these results, indicating that, in more than three-fourths of these materials, taken at random, there exist the equivalents of from 1 to 12, or more, per cent. of pentaglucofcs, plainly prove the common and abundant occurrence of the latter. It is evident, therefore, that among the vegetable products usually classed as carbohydrates the pentaglucofcs, or the gums giving rise to them, play an important part.

#### *B.—Quantitative Reduction of Fehling's Solution by the Pentaglucofcs.*

Both arabinose and xylose reduce Fehling's solution strongly, but their quantitative relation to it has not previously been studied, with the exception of a brief mention by Bauer of some limited determinations for arabinose, from which he concluded that it possessed in a slight degree greater reducing power than dextrose.<sup>1</sup>

<sup>1</sup> Landwirthschaftliche Versuch-Stationen 36, 304.

In view of the common occurrence of the pentaglucoſes, as already pointed out, it is evident that in the quantitative examination of any material for carbohydrates by hydrolytic methods, *i. e.* by inversion with acids and titration of the glucose thus formed with Fehling's solution, we may be dealing not only with the true glucoses derived from starch, cane sugar, etc., but also with more or less of one or both of the pentaglucoſes, since we know that the gums from which the latter are derived easily undergo hydrolytic change by the action of acids. Such analytical results may, therefore, be erroneous from two causes: first, from the assumption that the reduction of Fehling's solution is due solely to the presence of the true glucoses; or, second, from the assumption that the pentaglucoſes, when present, reduce Fehling's solution in the same degree as the true glucoses.

Take, for example, such a material as brewers' grains, in which it might be desired to ascertain the thoroughness of malting and fermentation by determining the residual carbohydrates. Such material might contain no trace of starch or sugar and yet might give abundant indications of the presence of these substances after inversion, because it contains so large an amount of the pentaglucoſe bodies that it is possible to isolate from it 2 per cent., or more, of the crystallised pentaglucoſes.<sup>1</sup>

It seemed important, therefore, to know the relations existing between these bodies and the true glucoses, and I have therefore determined the comparative values of arabinose and dextrose in dilute solutions toward Fehling's solution.

1. *Arabinose*.—The material used was prepared by me from cherry gum, and was pure, as was shown by its specific rotation ( $[\alpha]_D = 104.1^\circ$ ). From this material, solutions of 1,  $\frac{3}{4}$ ,  $\frac{1}{2}$  and  $\frac{1}{4}$  per cent. strength were made. The Fehling's solution was prepared according to the standard formula, *viz.* 34.639 grams of hydrous copper sulphate dissolved to a volume of 500 cc., and 60 grams sodium hydrate with 173 grams sodium-potassium tartrate dissolved to a volume of 500 cc., the two solutions being preserved separately, and mixed in equal volumes just before using. The determinations were made gravimetrically, as follows:

70 cc. of the Fehling's solution were brought to boiling, and exactly 25 cc. of the arabinose solution quickly run in from a full pipette, after which the whole was kept over the flame exactly four

<sup>1</sup> Ann. Chem. (Liebig) 249, 241.

minutes, of which the first fifty to sixty seconds were consumed in bringing the liquid to boiling again. The time of boiling and filtering was observed carefully. The precipitated cuprous oxide was collected on a Soxhlet asbestos filter with the aid of a pump, washed with boiling water, alcohol and ether, reduced to metallic copper in a current of dry hydrogen over a low flame, and, after cooling in hydrogen, weighed. The following are the results obtained:

*1-per cent. solution.*—25 cc., containing 0.250 gram arabinose, precipitated respectively:

1. 0.4850 gram copper.
2. 0.4874   “   “
3. 0.4860   “   “

An average of 0.48623 gram copper, or for 0.001 gram arabinose 0.001945 gram copper.

*$\frac{3}{4}$ -per cent. solution.*—25 cc., containing 0.1875 gram arabinose, precipitated respectively:

1. 0.3621 gram copper.
2. 0.3631   “   “
3. 0.3604   “   “

An average of 0.36187 gram copper, or for 0.001 gram arabinose 0.001929 gram copper.

*$\frac{1}{2}$ -per cent. solution.*—25 cc., containing 0.125 gram arabinose, precipitated respectively:

1. 0.2446 gram copper.
2. 0.2430   “   “
3. 0.2479   “   “

An average of 0.2448 gram copper, or for 0.001 gram arabinose 0.001958 gram copper.

*$\frac{1}{4}$ -per cent. solution.*—25 cc., containing 0.0625 gram of arabinose, precipitated respectively:

1. 0.1264 gram copper.
2. 0.1248   “   “
3. 0.1250   “   “

An average of 0.1254 gram copper, or for 0.001 gram arabinose 0.002 gram copper.

From this it appears that in solutions of 1 per cent., or less, strength, 1 milligram of arabinose precipitates 1.9–2 milligrams of copper.

2. *Xylose*.—The material used was prepared from wheat straw, and was of the desired purity, as shown by its specific rotation ( $[\alpha]_D = 18.41^\circ$ ).<sup>1</sup> The determinations were made under conditions as nearly as possible identical with those for arabinose, with the following results:

1-per cent. solution.—25 cc., containing 0.250 gram xylose, precipitated respectively:

1. 0.4686 gram copper.
2. 0.4640   "   "
3. 0.4667   "   "

An average of 0.4664 gram copper, or for 0.001 gram xylose 0.001864 gram copper.

$\frac{1}{4}$ -per cent. solution.—25 cc., containing 0.1875 gram xylose, precipitated respectively:

1. 0.3444 gram copper.
2. 0.3446   "   "
3. 0.3462   "   "

An average of 0.3451 gram copper, or for 0.001 gram xylose 0.001841 gram copper.

$\frac{1}{2}$ -per cent. solution.—25 cc., containing 0.125 gram xylose, precipitated respectively:

1. 0.2378 gram copper.
2. 0.2366   "   "
3. 0.2381   "   "

An average of 0.2375 gram copper, or for 0.001 gram xylose 0.0019 gram copper.

$\frac{1}{4}$ -per cent. solution.—25 cc., containing 0.0625 gram xylose, precipitated respectively:

1. 0.1235 gram copper.
2. 0.1222   "   "
3. 0.1217   "   "

An average of 0.1224 gram copper, or for 0.001 gram xylose 0.001959 gram copper.

Under the stated conditions, therefore, 1 milligram of xylose precipitates 1.86–1.959 milligrams of copper.

Dextrose, the most strongly reducing glucose heretofore

<sup>1</sup> This unusually fine preparation was kindly furnished me by Dr. E. W. Allen, of Washington, D. C., who prepared it himself, and to whom my thanks are due.

studied, precipitates, under similar conditions, 1.8–1.9 milligrams copper, or slightly less than the pentaglucooses. Stated in another way, the amounts of the different sugars in 1-per cent. solution required to precipitate the entire copper from 1 cc. of Fehling's solution are :

Arabinose, . . . . .	.004523 gram. <sup>1</sup>
Xylose, . . . . .	.004617 “
Dextrose, . . . . .	.004753 “
Levulose, . . . . .	.005144 “
Invert sugar, . . . . .	.004941 “
Galactose, . . . . .	.005110 “
Milk sugar, . . . . .	.006757 “
Maltose, . . . . .	.007780 “

From this it appears that the two pentaglucooses are the most strongly reducing sugars yet studied, and this is particularly true of arabinose. Both differ from the value for invert sugar sufficiently seriously to affect the accuracy of analyses in which they are concerned but not recognised.<sup>2</sup>

### C.—*Fermentability of the Pentaglucooses.*

In connection with the history of arabinose, mention is made by various investigators of its behavior toward fermenting agents, in which it is regarded as not subject to alcoholic fermentation. In some earlier studies of this body by Prof. Tollens and myself this view was substantiated, and it was further shown that this was a specific property of arabinose, in contradistinction from the true glucoses, galactose, levulose and dextrose, which are all fermentable, some conflicting views regarding galactose being at that time cleared up.<sup>3</sup>

In his original paper, in which the discovery of xylose was announced, Koch described the same as non-fermentable, which was somewhat remarkable if it were a true glucose, as was at that time supposed. Its identity as a pentaglucoose being afterwards established, it was of importance to show that it is, like arabinose, strictly non-fermentable, thus fixing this as a character of the

<sup>1</sup> Tollens : *Handbuch der Kohlenhydrate*, p. 284.

<sup>2</sup> H. Ost (Ber. d. chem. Ges. **23**, 3006) notes the reducing effect of arabinose on a solution of potassium-copper carbonate, and finds its value lower than that of dextrose, but higher than that of galactose, toward this reagent.

<sup>3</sup> Ann. Chem. (Liebig) **249**, 257; and Ber. d. chem. Ges. **21**, 1572.



$C_5H_{10}O_5$  group. In order to determine the non-fermentability of a given substance it is very essential that such a fermentation-test shall be made under conditions favorable to the requirements and activity of the yeast-plant used. No better example of this is known than that of galactose, which has been reported non-fermentable by some experimenters, who seemed to have worked with poorly nourished yeast or that deficient in vitality. Where there has been due regard for these conditions, galactose will produce nearly theoretical results of fermentation, although it is plain that it is less rapidly and easily subject to the influence of yeast than its isomers, levulose and dextrose. The method used for xylose was the same as that formerly applied to arabinose. Its special feature consists in supplying the yeast used with a nutrient extract, made by boiling 100 cc. of the semi-fluid brewery yeast with 100 cc. of water and filtering off the dark-brown extract resulting. Such a solution contains the natural constituents of the yeast, and, as a nutrient, seems to give better results than artificially prepared solutions of salts.

In the study of xylose two sets of experiments were performed. In one the carbon dioxide produced was collected, and in the other the alcohol. The former were conducted in eudiometer tubes which were first filled to within 15 cc. of their capacity with mercury; then were added 5 cc. of distilled water, 5 cc. of the above-described nutrient solution, 5 cc. of a mixture of 5 grams of Fleischmann's compressed yeast with 50 cc. of water, and, lastly, the weighed xylose. The tube was then inverted in a mercury trough, and the gaseous products of fermentation were allowed to collect in the upper end. A second tube filled in exactly the same way, but containing cane sugar instead of xylose, was arranged for comparison and as an index of the activity of the yeast.

For the first experiment were taken 0.139 gram xylose and 0.1566 gram cane sugar. Within a quarter of an hour lively fermentation had begun in the cane-sugar solution, and after ten hours seemed practically complete. In the xylose solution no action was observed. After six days, no farther action being noticeable, the necessary readings were taken for calculating the amount of gas collected (including that absorbed by the liquid) from the cane sugar. Less than 0.5 cc. of gas had collected on the xylose solution, too little to indicate any appreciable fermentative

action. The gas produced from the cane sugar was wholly absorbed by potassium hydrate solution, and was therefore carbon dioxide. Reducing the temperature and pressure to  $0^{\circ}$  and 760 mm., the volume of the undissolved gas from cane sugar was 31.07 cc., and of that absorbed in the solution, 13.16 cc., or a total of 44.23 cc., equal to 78.7736 milligrams, or 50.49 per cent. of the sugar used.

In the second experiment were taken 0.1526 gram of cane sugar and 0.1572 gram xylose under the same conditions as before. In this case also the cane sugar underwent active fermentation, but no action was observed in the xylose solution. After seven days, measurements of the gas from the cane sugar, which was found to be carbon dioxide, gave a total of 78.506 milligrams, or 51.5 per cent.

The yield of alcohol was next determined in a third experiment. 1 gram each of xylose and cane sugar was placed in flasks of about 200 cc. capacity, with 35 cc. of water, 5 cc. of the nutrient fluid and 10 cc. of the yeast mixture. The flasks were closed with a water-valve. As in the other cases, the cane sugar showed active fermentation, but no action was detected in the xylose. After five days both solutions were neutralised with sodium carbonate, and after slight dilution, 50 cc. distilled off and the alcohol determined in the distillates by taking their specific gravities with a Sprengel's specific-gravity flask.

50 cc. of distillate from the cane-sugar solution had the specific gravity 0.9982, equal to 0.472 gram alcohol, or 47.2 per cent.

50 cc. of distillate from the xylose solution had the specific gravity 0.9999, showing no appreciable amount of alcohol present.

Summing up the results of these experiments, we have:

	Carbon-dioxide.	Alcohol.
1. { Xylose,	...	...
{ Cane sugar,	50.49 per cent.	...
2. { Xylose,	...	...
{ Cane sugar,	51.50     "	...
3. { Xylose,	...	...
{ Cane sugar,	...	47.20 per cent.
Calculated for $C_{12}H_{22}O_{11}$ ,	51.46     "	48.54     "

From this it appears that under those conditions which produced almost theoretical fermentation of cane sugar, xylose did not ferment in the least. It is therefore, like its isomer arab-

inose, non-fermentable, and this becomes a specific characteristic of the pentaglucooses.

It seems, therefore, that the pentaglucooses are of abundant occurrence in nature in the form of gum-like constituents of vegetable tissues; that these bodies are easily converted into the pentaglucooses themselves, and in such form are liable to be confused with the true glucoses, from which, however, they have quite different analytical, and as far as we know, economic values. In addition to the furfurol reaction, non-fermentability seems to be a further distinguishing property of the pentaglucooses.

In view of the importance of this group, a method by which they may be determined quantitatively in the presence of the true glucoses seems desirable. Such a method has lately been proposed by Günther and Tollens.<sup>1</sup> Simultaneously with them I have been engaged upon the same subject with somewhat similar results, a more extended report of which is for the present reserved.

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## ON THE ACTION OF AMMONIA AND ALKYLAMINES ON ETHYLIC ACETOSUCCINATE AND SUBSTITUTED ETHYLIC ACETOSUCCINATES.

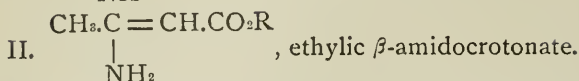
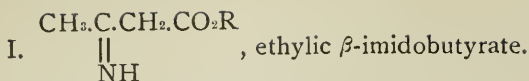
BY WILLIAM ORREN EMERY.

The following research was undertaken for the purpose of finding, if possible, a general method by which unsaturated  $\gamma$ -lactams might be prepared, and, at the same time, of affording further proofs of the constitution of the products formed by the action of ammonia and alkylamines on compounds analogous to ethylic acetoacetate. Although the investigation has by no means been brought to an end, still it was thought expedient to offer the results thus far obtained.

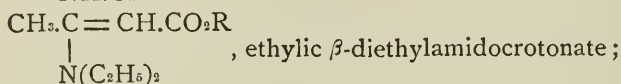
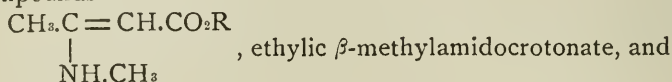
The action of ammonia and alkylamines on ethylic acetoacetate has been, for many chemists, a fruitful field for experiment. The facts gathered by Collie<sup>2</sup> with regard to the action of ammonia on ethylic acetoacetate were insufficient to determine the constitution of the product formed by this reaction. One had the choice between the two formulæ :

<sup>1</sup> Ber. d. chem. Ges. 23, 1751.

<sup>2</sup> Ann. Chem. (Liebig) 226, 294.



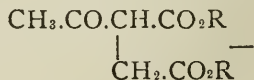
Not until Kuckert<sup>1</sup> had, by the action of methylamine and diethylamine on ethylic acetoacetate, succeeded in preparing the compounds



and, further, not until Conrad and Epstein<sup>2</sup> had observed that, by the action of ammonia on ethylic acetodiethylacetate,  $\text{CH}_3.\text{CO}.\text{C}(\text{C}_2\text{H}_5)_2.\text{CO}_2\text{R}$ , as well as on ethylic acetodichloracetate,  $\text{CH}_3.\text{CO}.\text{CCl}_2.\text{CO}_2\text{R}$ , no amido-derivative resulted; did it become evident that only formula II could be the correct one. There can, therefore, be no question that ammonia and alkylamines act in the same way on ethylic acetoacetate. The resulting products of this reaction must be regarded as derivatives of ethylic  $\alpha$ -crotonate,  $\text{CH}_3.\text{CH}=\text{CH}.\text{CO}_2\text{R}$ .

In the case of ethylic acetoacetate we have an example of an ether of a  $\beta$ -ketonic acid which, as we have seen, forms with ammonia ethylic  $\beta$ -amidocrotonate. It has been, thus far, impossible to bring about in this latter compound an intermolecular condensation. If we now turn our attention to an ether of a  $\gamma$ -ketonic acid, we shall find that ethylic acetopropionate,  $\text{CH}_3.\text{CO}.\text{CH}_2.\text{CH}_2.\text{CO}_2\text{R}$ , is the simplest example of this kind. The behavior of this ether towards ammonia has already been investigated by Wolff,<sup>3</sup> who found the resulting product of this reaction to be the so-called acetopropionamide, which, according to Wolff, has the constitution represented by the formula  $\text{CH}_3.\text{CO}.\text{CH}_2.\text{CH}_2.\text{CO}.\text{NH}_2$ . This amide does not appear capable of undergoing condensation.

If we now consider for a moment the ether of a dibasic ketonic acid—for example, ethylic acetosuccinate,

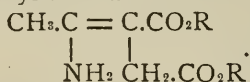


<sup>1</sup> Ber. d. chem. Ges. **18**, 618.

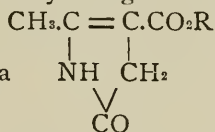
<sup>2</sup> Ibid. **20**, 3056.

<sup>3</sup> Ann. Chem. (Liebig) **229**, 262.

we have at once the ether of a  $\beta$ - and a  $\gamma$ -ketonic acid. Conrad and Epstein<sup>1</sup> have already made a short study of the action of ammonia on ethylic acetosuccinate, and have succeeded in preparing the so-called ethylic amidoacetosuccinate,

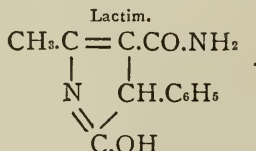
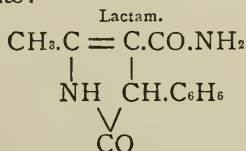


It will be readily seen from the formula above that the amido-rest occupies the  $\beta$ -position to the one carboxyl-group, the  $\gamma$ -position to the other. If under favorable conditions it were possible to split off the elements of alcohol from this compound, the most reasonable supposition would be that the condensation would take place between the amido-rest and that carboxyl-group occupying the  $\gamma$ -position to it. Experiment has shown that the condensation does indeed result in the manner indicated. The product formed by the action of ammonia on ethylic acetosuccinate loses alcohol quite readily, and is thereby changed to the compound



having the constitutional formula

Similar results were obtained by Weltner,<sup>2</sup> who investigated the action of ammonia in the heat on ethylic acetophenylsuccinate,  $\text{CH}_3.\text{CO}.\text{CH}.\text{CO}_2\text{R}$   
 $\quad \quad |$   
 $\quad \quad \text{C}_6\text{H}_5.\text{CH}.\text{CO}_2\text{R}$ , and found that, among other things, a substance was formed which must have one of the two following formulæ:



Weltner was unable to decide from his experiments which of the two formulæ was the correct one.

From the above the question naturally arises: (a) Is it possible to generalise this reaction? and (b) is it possible to furnish conclusive proof which shall establish with certainty the lactam or the lactim formula?

<sup>1</sup> Ber. d. chem. Ges. 20, 3058.

<sup>2</sup> Ibid. 18, 793.



In an endeavor to bring about a solution of these problems I have carried out the following series of experiments:

- I. Ammonia and ethylic acetosuccinate.
- II. Methylamine and ethylic acetosuccinate.
- III. Ethylamine    "       "       "
- IV. Propylamine   "       "       "
- V. Isobutylamine "       "       "
- VI. Amylamine     "       "       "
- VII. Ammonia       "       "       acetomethylsuccinate.
- VIII. Ammonia      "       "       acetophenylsuccinate.

In every case in which ammonia was used it was employed in the form of an alcoholic solution saturated at  $0^{\circ}$ . An aqueous solution of ammonia was discarded for the reason that its saponifying action on carbethoxyl-rests would be greater than that of the alcohol solution, and such an action I desired if possible to avoid. As my chief object in this research was an examination of the end-products which arise by the action of ammonia and alkylamines on the above-mentioned ketonic ethers, I have in general paid but little attention to the intermediate products formed by this reaction.

### I.—*Ammonia and Ethylic Acetosuccinate.*<sup>1</sup>

Ammonia and ethylic acetosuccinate unite readily in alcoholic solution. The reaction may be conveniently performed as follows: One volume of ethylic acetosuccinate is gradually mixed with two volumes of a solution of ammonia in absolute alcohol saturated at  $0^{\circ}$ . The mixture is kept in a small well-corked flask and allowed to stand 24 hours in a cool place, after which it is poured into a shallow dish in order that it may evaporate slowly at the ordinary temperature. In about 24 hours the contents of the evaporating dish have become a mass of large transparent crystals. These are first freed from the small amount of mother-liquor which accompanies them, by spreading on porous plates, and are then recrystallised once or twice from warm ethyl acetate.

<sup>1</sup> In preparing the ethylic acetosuccinate used in the following experiments from ethylic sodiumacetoacetate, I have found it more expedient to employ bromacetic ether in place of the more common chlorine-compound, from the fact that the former is more readily acted upon by ethylic sodiumacetoacetate than chloracetic ether, and the result is a far better yield of ethylic acetosuccinate. Great care must, however, be taken to cool well on bringing together the alcoholic solution of ethylic sodiumacetoacetate and bromacetic ether, since the reaction takes place almost instantly, and, indeed, with the evolution of much heat. Bromacetic acid may be conveniently made according to the method of Michael (this Journal 5, 202).



Large, transparent, highly refractive crystals were obtained which melt at  $62^{\circ}$ .<sup>1</sup> The analysis gave the following results :

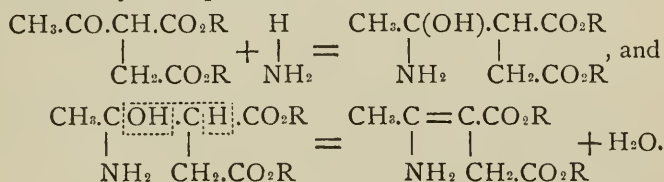
I. 0.2007 gram substance gave 0.4120 gram  $\text{CO}_2$  and 0.1478 gram  $\text{H}_2\text{O}$ .<sup>2</sup>

II. 0.1311 gram substance gave 0.2686 gram  $\text{CO}_2$  and 0.0932 gram  $\text{H}_2\text{O}$ .

III. 0.2805 gram substance gave the following data:  $B = 746$ ,  $t = 13^{\circ}$ ,  $v = 15.8$  cc.

	Calculated for $\text{C}_{10}\text{H}_{17}\text{NO}_4$ .	I.	Found. II.	III.
C	55.81	55.98	55.88	...
H	7.91	8.18	7.90	...
N	6.51	...	...	6.53
O	29.77	...	...	...

For reasons which will be discussed further on, I would propose the name " $\alpha$ -amidoethylidenesuccinic ether" for the compound obtained by the action of ammonia on ethylic acetosuccinate. Its formation evidently takes place in two phases perfectly analogous to the formation of  $\beta$ -amidocrotonic ether, and may be represented by the equations:



$\alpha$ -Amidoethylidenesuccinic ether is readily soluble in alcohol, ether and chloroform, less so in ethyl acetate and carbon bisulphide, and insoluble in cold water. On heating with acetic anhydride in slight excess for several hours at  $155^{\circ}$ – $160^{\circ}$ , an acetyl derivative was formed. The product was purified by washing first with water, then with a dilute solution of sodium carbonate, after which it was taken up with ether, the ethereal solution dried over calcium chloride, and the ether finally evaporated in a vacuum desiccator. In this way a thick, bright straw-colored oil was obtained which on analysis gave the following figures :

I. 0.1507 gram substance gave 0.3115 gram  $\text{CO}_2$  and 0.1018 gram  $\text{H}_2\text{O}$ .

<sup>1</sup> Conrad u. Epstein: Ber. d. chem. Ges. 20, 3058.

<sup>2</sup> All the combustions were performed in a tube open at both ends.

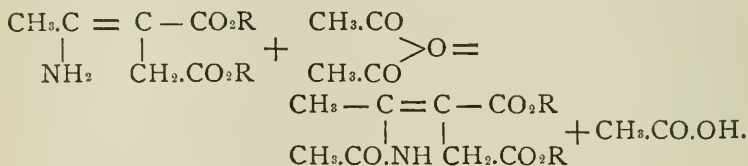
II. 0.2266 gram substance gave 0.4664 gram  $\text{CO}_2$  and 0.1513 gram  $\text{H}_2\text{O}$ .

III. 0.3075 gram substance gave the following data:  $B = 744.5$ ,  $t = 13^\circ$ ,  $v = 14.5$  cc.

IV. 0.2161 gram substance gave 0.4446 gram  $\text{CO}_2$  and 0.1458 gram  $\text{H}_2\text{O}$ .<sup>1</sup>

	Calculated for $\text{C}_{12}\text{H}_{19}\text{NO}_5$	I.	II.	Found.	III.	IV.
C	56.03	56.37	56.13	...	...	56.11
H	7.39	7.50	7.42	...	...	7.49
N	5.45	...	...	...	5.52	...
O	31.13	...	...	...	...	...

This substance, for which I propose the name " $\alpha$ -acetyl-amidoethylidenesuccinic ether," is formed in a way exactly analogous to that of  $\beta$ -acetylamidocrotonic ether<sup>2</sup> from  $\beta$ -amidocrotonic ether, according to the equation:



The new compound may be distilled under greatly diminished pressure without decomposition. Under a pressure of about 11 mm. the boiling point is  $175^\circ$ – $176^\circ$  (temperature of paraffin-bath  $195^\circ$ ). The specific gravity was found to be

$$d_{40}^{20} = 1.12873.$$

The behavior of  $\alpha$ -amidoethylidenesuccinic ether on heating is of great interest, as showing its capability of being changed into a lactam of the formula  $\text{C}_8\text{H}_{11}\text{NO}_3$ . The operation may be conveniently performed as follows: The amido ether is heated in a paraffin-bath at  $145^\circ$ – $150^\circ$  until the vapors of alcohol cease to be given off. On cooling the product becomes a viscous mass, and generally shows but little inclination to crystallise. It is now dissolved in warm ether and the latter allowed to evaporate in a

<sup>1</sup> Combustion IV was made from the substance after it had been distilled.

<sup>2</sup> Collie: Ann. Chem. (Liebig) **226**, 309. I wish to take this opportunity of pointing out the probable identity of  $\beta$ -acetylamidocrotonic ether with the so-called  $\beta$ -acetylamidobutyric ether, which Canzoneri and Spica (Gazz. chim. ital. **14**, 491) obtained by the action of acetamide on ethylic acetoacetate. Beilstein evidently regards these two substances as different, as he gives them twice in his hand-book, 2d edition, I, 542, 543.

vacuum desiccator. The crystals, consisting of needles, are freed from the mother-liquor by drying on porous plates, and are then purified by repeated crystallisation from warm ether. After one or two recrystallisations, fine snow-white needles are obtained which melt at  $133^{\circ}$ – $134^{\circ}$ . The same substance is formed when  $\alpha$ -amidoethylidenesuccinic ether is distilled under greatly diminished pressure. By rapid distillation the greater part of the  $\alpha$ -amidoethylidenesuccinic ether passes over unchanged; if, on the other hand, the distillation be allowed to take place slowly, a portion goes over unchanged, while another loses alcohol and distils as a thick colorless oil which gradually solidifies to snow-white needles. The boiling point was observed to be  $195^{\circ}$  (temperature of the paraffin-bath  $215^{\circ}$ – $220^{\circ}$ ) under a pressure of about 12 mm. The lactam, if prepared in this way, needs only one recrystallisation from warm ether in order to be brought into a state of absolute purity. Analysis gave the following figures:

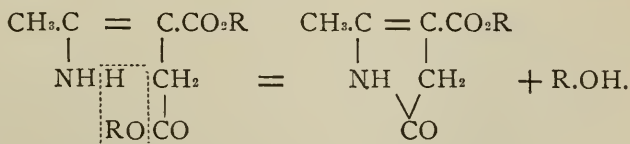
I. 0.1361 gram substance gave 0.2841 gram  $\text{CO}_2$  and 0.0830 gram  $\text{H}_2\text{O}$ .

II. 0.1313 gram substance gave 0.2744 gram  $\text{CO}_2$  and 0.0782 gram  $\text{H}_2\text{O}$ .

III. 0.2017 gram substance gave the following data:  $B=746$ ,  $t=13^{\circ}$ ,  $v=14.5$  cc.

	Calculated for $\text{C}_8\text{H}_{11}\text{NO}_3$ .	I.	Found. II.	III.
C	56.80	56.93	56.99	...
H	6.51	6.77	6.62	...
N	8.28	...	...	8.33
O	28.40	...	...	...

$\alpha$ -Amidoethylidenesuccinic ether is therefore converted into its lactam, according to the equation:



The new substance is easily soluble in alcohol, more sparingly in ether and carbon bisulphide, and may be recrystallised from water. If it be treated with a solution of sodic ethylate in perfectly dry alcohol-ether, a white insoluble sodic compound is formed which very soon deliquesces when exposed to the air.

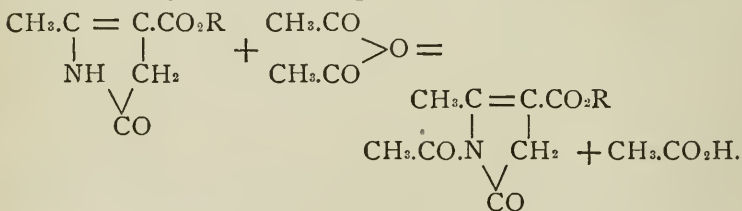
Bromine gives in a solution of carbon bisulphide a crystalline product, which has not yet been further examined. If the lactam be heated a few hours at  $155^{\circ}$ – $160^{\circ}$  in a sealed tube with an excess of acetic anhydride, a small quantity of an acetyl compound is formed. This gradually separates in the form of a sandy powder from the brown-colored liquid obtained by heating, and may be conveniently freed from the mother-liquor by drying on a porous plate. After one recrystallisation from ether it was obtained as a white powder, melting at  $141^{\circ}$ – $142^{\circ}$ , and on analysis gave the following figures:

I. 0.1882 gram substance gave the following data:  $B=750$ ,  $t=15^{\circ}$ ,  $v=10.9$  cc.

II. 0.1509 gram substance gave the following data:  $B=752$ ,  $t=19^{\circ}$ ,  $v=9$  cc.

	Calculated for $C_{10}H_{13}NO_4$ .	I.	Found.	II.
C	56.87	...	...	...
H	6.16	...	...	...
N	6.64	6.69	6.69	6.78
O	30.33	...	...	...

The acetyl compound has therefore the formula  $C_{10}H_{13}NO_4$ . It is produced from the lactam of  $\alpha$ -amidoethylidenesuccinic ether and acetic anhydride, according to the equation



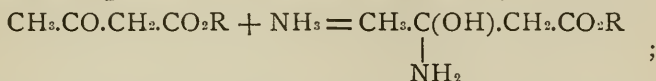
## II.—Methylamine and Ethylic Acetosuccinate.

So far as the yield of lactam by the action of alkylamines on ethylic acetosuccinate is concerned, these bases may be used either in the pure state or in the form of an absolute-alcoholic solution. In every case the substances unite readily, while the yield of lactam approaches very nearly that of the theory. From the investigations of Collie<sup>1</sup> and of Kuckert,<sup>2</sup> it appears extremely probable that the former observed the formation of the first

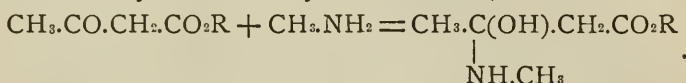
<sup>1</sup>Ann. Chem. (Liebig) **226**, 298.

<sup>2</sup>Ber. d. chem. Ges. **18**, 618.

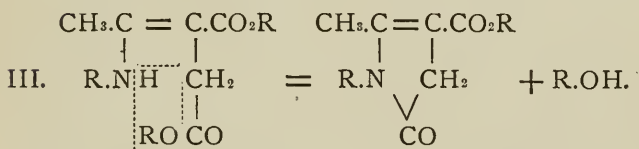
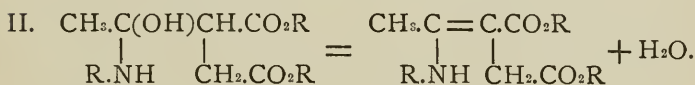
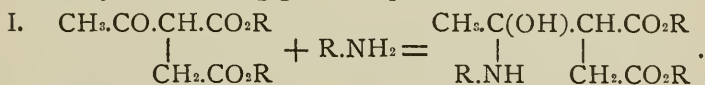
product arising from the action of ammonia on ethylic acetoacetate,



and the latter the formation of the first product formed by the action of methylamine on ethylic acetoacetate,



Owing, however, to the great instability of these compounds it was found impossible to analyse them. Although, by the action of alkylamines on ethylic acetosuccinate, I have in no case been able to isolate the intermediate products, still I believe the reaction takes place in a perfectly analogous way, and may be represented by the following general equations:



In order to prepare the methylamine derivative of ethylic acetosuccinate I operated as follows: ethylic acetosuccinate was dissolved in twice the volume of absolute alcohol, and this solution saturated with somewhat more than the calculated amount of methylamine. This mixture, after being kept in a cool place for 24 hours, was then allowed to evaporate in an open dish at the ordinary temperature. However, as the product showed no tendency to crystallise, it was then fractioned under greatly diminished pressure. After alcohol and water had passed over, a thick, colorless oil was obtained which, under a pressure of about 11 mm., boiled constantly at 160° (temperature of paraffin-bath 185°), and gradually solidified to a very compact mass of snow-white crystals. The latter, upon recrystallisation from ether or carbon bisulphide, showed the melting point 42°, and gave the following figures on analysis:

I. 0.2005 gram substance gave 0.4349 gram  $\text{CO}_2$  and 0.1311 gram  $\text{H}_2\text{O}$ .

II. 0.1738 gram substance gave 0.3762 gram  $\text{CO}_2$  and 0.1134  $\text{H}_2\text{O}$ .

III. 0.2234 gram substance gave the following data:  $B = 749.5$ ,  $t = 11.5^\circ$ ,  $v = 14.8$  cc.

	Calculated for $\text{C}_8\text{H}_{13}\text{NO}_3$ .	I.	Found. II.	III.
C	59.02	59.23	59.06	...
H	7.10	7.26	7.25	...
N	7.65	...	...	7.70
O	26.23	...	...	...

The new substance is extremely soluble in ether and carbon bisulphide, in contrast to the lactam of  $\alpha$ -amidoethylidenesuccinic ether. On heating with acetic anhydride I was unable to obtain an acetyl derivative.

### III.—*Ethylamine and Ethylic Acetosuccinate.*

Ethylic acetosuccinate and ethylamine were mixed in equal molecular proportions, and to this mixture twice the volume of absolute alcohol was added. After standing about 24 hours in the cold, the yellow-colored product was fractioned under diminished pressure. When alcohol and water had been removed, a fraction was obtained which, under a pressure of about 14 mm., boiled constantly at  $165^\circ$  (temperature of paraffin-bath  $190^\circ$ ). On cooling the distillate slowly solidified to a snow-white mass of very fine needles, which, after one recrystallisation from carbon bisulphide, melted at  $75^\circ$ – $76^\circ$ , and on analysis gave the following figures:

I. 0.1510 gram substance gave 0.3352 gram  $\text{CO}_2$  and 0.1051 gram  $\text{H}_2\text{O}$ .

II. 0.1532 gram substance gave 0.3390 gram  $\text{CO}_2$  and 0.1061 gram  $\text{H}_2\text{O}$ .

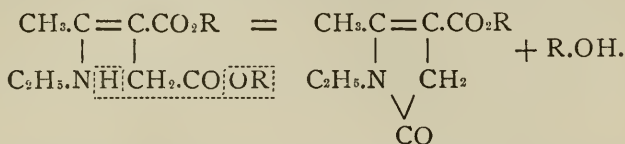
III. 0.2102 gram substance gave the following data:  $B = 759$ ,  $t = 19^\circ$ ,  $v = 13.2$  cc.

IV. 0.1836 gram substance gave the following data:  $B = 757.5$ ,  $t = 20^\circ$ ,  $v = 12$  cc.

	Calculated for $\text{C}_{10}\text{H}_{15}\text{NO}_3$ .	I.	Found. II.	III.	IV.
C	60.91	60.54	60.35	...	...
H	7.61	7.73	7.69	...	...
N	7.11	...	...	7.21	7.45
O	24.37	...	...	...	...



This new substance, which is the lactam of  $\alpha$ -ethylamidoethylidenesuccinic ether, is formed according to the following equation :



It is very similar in character to the preceding compound. In an attempt to regenerate the ether of which it is the lactam, by heating a short time with absolute alcohol, it was found that by far the greater part, if not all, had remained unchanged; for on evaporating the alcohol in a vacuum, colorless needles melting at  $75^\circ$ – $76^\circ$  were obtained. A nitrogen determination led to the formula  $\text{C}_{10}\text{H}_{15}\text{NO}_3$ . Further, it was found that the lactam is formed in part in the alcoholic solution of ethylamine and ethylic acetosuccinate. For example, such a solution, after remaining three days in the cold, was freed from alcohol and water in a vacuum, without the application of external heat. The residual liquid solidified in the form of a mass of needles. These, after being dried on a porous plate and recrystallised from carbon bisulphide, melted at  $75^\circ$ – $76^\circ$  and gave values which led to the formula  $\text{C}_{10}\text{H}_{15}\text{NO}_3$ . Combustion IV was made with the substance obtained in this way. The easy formation of the lactam, as above described, is quite remarkable, both in showing the great tendency of  $\alpha$ -ethylamidoethylidenesuccinic ether to go over into its lactam, and in explaining the unusual stability of the latter compound upon being heated with alcohol.

#### IV.—*Propylamine and Ethylic Acetosuccinate.*

These two substances unite with great readiness when mixed either in the pure state or in alcoholic solution. I have generally operated without the aid of alcohol. The mixture, on standing 24 hours, was found to have become cloudy, owing to the separation of water. This was separated mechanically from the remaining liquid and the latter purified by fractional distillation. The greater portion boiled constantly, under a pressure of about 14–15 mm., at  $172^\circ$  (temperature of paraffin-bath  $188^\circ$ ), and upon cooling solidified to a compact mass of snow-white needles. These, after one recrystallisation from carbon bisulphide, melted at  $50^\circ$  and gave the following figures on analysis :

I. 0.1500 gram substance gave 0.3434 gram  $\text{CO}_2$  and 0.1120 gram  $\text{H}_2\text{O}$ .

II. 0.1509 gram substance gave 0.3445 gram  $\text{CO}_2$  and 0.1114 gram  $\text{H}_2\text{O}$ .

III. 0.2009 gram substance gave the following data:  $B=759$ ,  $t=19^\circ$ ,  $v=12.5$  cc.

	Calculated for $\text{C}_{11}\text{H}_{17}\text{NO}_3$ .	I.	Found. II.	III.
C	62.56	62.45	62.26	...
H	8.06	8.29	8.19	...
N	6.63	...	...	6.89
O	22.75	...	...	...

#### V.—*Isobutylamine and Ethylic Acetosuccinate.*

10 grams of ethylic acetosuccinate were mixed with 3.4 grams of dry isobutylamine, and this yellow-colored mixture allowed to stand several days in the cold. At the end of two days a layer of water had collected on the upper surface of the liquid. The water was removed by means of a separating funnel and the residual liquid fractioned under diminished pressure. By far the greater part boiled constantly at  $175^\circ$  (temperature of paraffin-bath  $195^\circ$ ) under a pressure of 15 mm., and on cooling solidified to a crystalline mass of needles. After recrystallisation from carbon bisulphide, snow-white needles melting at  $68^\circ$  were obtained. Analysis gave figures corresponding to the formula  $\text{C}_{12}\text{H}_{19}\text{NO}_3$ , that is, the lactam of  $\alpha$ -isobutylamidoethylidenesuccinic ether.

I. 0.1528 gram substance gave 0.3597 gram  $\text{CO}_2$  and 0.1192 gram  $\text{H}_2\text{O}$ .

II. 0.1612 gram substance gave 0.3771 gram  $\text{CO}_2$  and 0.1243 gram  $\text{H}_2\text{O}$ .

III. 0.2020 gram substance gave the following data:  $B=760$ ,  $t=18^\circ$ ,  $v=11.5$  cc.

	Calculated for $\text{C}_{12}\text{H}_{19}\text{NO}_3$ .	I.	Found. II.	III.
C	64.00	64.20	63.79	...
H	8.44	8.67	8.57	...
N	6.22	...	...	6.57
O	21.33	...	...	...

VI.—*Amylamine and Ethylic Acetosuccinate.*

10 grams of ethylic acetosuccinate and 4 grams of amylamine were mixed with 5 cc. of absolute alcohol. This mixture, after standing two days at the ordinary temperature, was fractioned under diminished pressure. After alcohol and water had passed over, a fraction, boiling at  $188^{\circ}$  (temperature of paraffin-bath  $205^{\circ}$ ) under a pressure of 16 mm., was obtained which, on cooling, gradually solidified to a snow-white mass of crystalline leaves. Upon recrystallisation from carbon bisulphide, colorless leaves, melting at  $51^{\circ}$ – $52^{\circ}$ , were obtained. These gave on analysis the following figures:

I. 0.1505 gram substance gave 0.3590 gram  $\text{CO}_2$  and 0.1210 gram  $\text{H}_2\text{O}$ .

II. 0.1501 gram substance gave 0.3589 gram  $\text{CO}_2$  and 0.1204 gram  $\text{H}_2\text{O}$ .

III. 0.2006 gram substance gave the following data:  $B = 761$ ,  $t = 19^{\circ}$ ,  $v = 10.7$  cc.

	Calculated for $\text{C}_{13}\text{H}_{21}\text{NO}_3$ .	I.	Found. II.	III.
• C	65.27	65.06	65.21	...
H	8.78	8.93	8.91	...
N	5.86	...	...	6.14
O	20.08	...	...	...

This substance is, as is shown by the above, the lactam of  $\alpha$ -amylamidoethylidenesuccinic ether.

All the foregoing *substituted* lactams are extremely soluble in ether and carbon bisulphide, and, with the exception of the amyl derivative, crystallise in needles. If not perfectly pure they show a tendency to become yellow on keeping, and when treated with a dilute solution of barium hydrate they appear to suffer decomposition.

VII.—*Ammonia and Ethylic Acetomethylsuccinate.*

Ethylic acetomethylsuccinate was mixed with twice its volume of alcoholic ammonia saturated at  $0^{\circ}$ , and, after standing two days in a well-corked flask, the mixture was allowed to evaporate at the ordinary temperature. In the course of a few days the thick oily product began to crystallise very slowly until finally the whole became a mass of fine crystals. These were spread on

porous plates in order to free them from the mother-liquor. After two recrystallisations from warm acetic ether, in which the new substance is sparingly soluble, snow-white crystals, melting at  $127^{\circ}$ , were obtained. The analysis gave the following results:

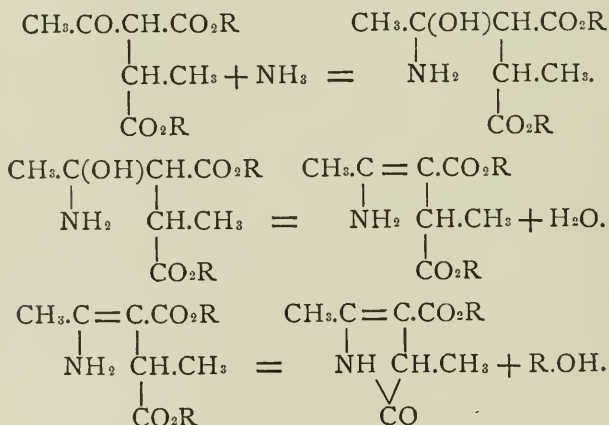
I. 0.2010 gram substance gave the following data:  $B=755$ ,  $t=17^{\circ}$ ,  $v=13.7$  cc.

II. 0.2002 gram substance gave the following data:  $B=755$ ,  $t=21^{\circ}$ ,  $v=14$  cc.

III. 0.1511 gram substance gave 0.3288 gram  $\text{CO}_2$  and 0.1010 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_9\text{H}_{13}\text{NO}_3$ .	I.	Found. II.	III.
C	59.02	...	...	59.34
H	7.10	...	...	7.42
N	7.65	7.85	7.89	...
O	26.23	...	...	...

The substance, therefore, has the formula  $\text{C}_9\text{H}_{13}\text{NO}_3$ , and is the lactam of  $\alpha$ -amidoethylidenemethylsuccinic ether. Its formation may be represented by the equations



The new compound is isomeric with that lactam which is formed by the action of methylamine on ethylic acetosuccinate. It appears quite remarkable that the formation of the amido-ether as intermediate product in this reaction remained unnoticed. The great tendency to lactam-formation, by which alcohol is split off, evidently depends upon the presence of the methyl-rest.

VIII.—*Ammonia and Ethylic Acetophenylsuccinate.*

Ethylic acetophenylsuccinate is described by Weltner<sup>1</sup> as crystallising in plates which melt at 75°–76°. I have prepared this ether by the action of phenylbromacetic ether on ethylic sodium-acetoacetate, and have invariably observed it in the form of needles, melting, as above, at 75°–76°.

By the action of alcoholic ammonia on ethylic acetophenylsuccinate, I found it convenient to use two volumes of the former and one of the latter. Both are kept in a well-corked flask, which from time to time is shaken vigorously in order to bring about a solution of the ether in the alcoholic ammonia. This is generally effected in about two days, after which the solution is allowed to evaporate in open dishes. Diamond-shaped plates soon begin to separate from the liquid until finally the whole becomes a mass of crystals. These may be freed from the mother-liquor by drying on porous plates. After several recrystallisations from hot acetic ether, in which the substance is soluble with difficulty, snow-white crystals, melting at 147°–149°, were obtained. It was, however, observed that if the substance be very slowly heated to 127°–128° and there held for a few moments, the substance melted at that temperature. The analysis gave the following results:

I. 0.1530 gram substance gave 0.3603 gram CO<sub>2</sub> and 0.0915 gram H<sub>2</sub>O.

II. 0.1205 gram substance gave 0.2840 gram CO<sub>2</sub> and 0.0737 gram H<sub>2</sub>O.

III. 0.1500 gram substance gave 0.3538 gram CO<sub>2</sub> and 0.0906 gram H<sub>2</sub>O.

IV. 0.1509 gram substance gave 0.3565 gram CO<sub>2</sub> and 0.0902 gram H<sub>2</sub>O.

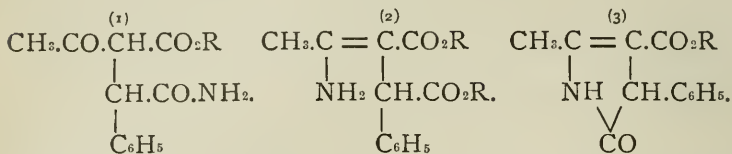
V. 0.1509 gram substance gave 0.3562 gram CO<sub>2</sub> and 0.0902 gram H<sub>2</sub>O.

VI. 0.2022 gram substance gave the following data:  $B = 758.5$ ,  $t = 19^\circ$ ,  $v = 9.8$  cc.

	Calculated for			Found.					
	(1) C <sub>14</sub> H <sub>17</sub> NO <sub>4</sub>	(2) C <sub>16</sub> H <sub>21</sub> NO <sub>4</sub>	(3) C <sub>14</sub> H <sub>15</sub> NO <sub>3</sub>	I.	II.	III.	IV.	V.	VI.
C	63.87	65.98	68.57	64.22	64.28	64.33	64.43	64.37	...
H	6.46	7.21	6.12	6.64	6.79	6.71	6.64	6.64	...
N	5.32	4.81	5.71	...	...	...	...	...	5.56
O	24.33	21.99	19.59	...	...	...	...	...	...

<sup>1</sup> Ber. d. chem. Ges. 17, 71.

The empirical formulæ represent three of the possible compounds which might be formed by the action of ammonia on ethylic acetophenylsuccinate, namely :



The results of analysis do not, however, show the necessary degree of conformity with any of these formulæ ; it is therefore probable that the substance is either difficult to obtain in a state of purity or not easy of combustion. The readiness with which it gives the lactam [formula (3)] on heating confirms the belief that it must be constituted either according to formula (1) or according to formula (2). Which of the two is the correct one I have as yet been unable to decide.

In order to prepare the lactam, the product obtained by the action of ammonia on the ethylic acetophenylsuccinate is heated for a short time at  $160^\circ$  in a paraffin-bath, or until the evolution of alcohol vapors has ceased. It is then dissolved in hot acetic ether, in which it is sparingly soluble, and from this medium crystallises in snow-white needles. Two recrystallisations are generally necessary, before the substance can be obtained in a state of purity. It melts at  $127^\circ$ – $128^\circ$ , is quite readily soluble in alcohol and in ether, more sparingly in ethylic acetate and carbon bisulphide. Analysis led to the formula  $\text{C}_{14}\text{H}_{15}\text{NO}_3$ .<sup>1</sup>

I. 0.1238 gram substance gave 0.3130 gram  $\text{CO}_2$  and 0.0718 gram  $\text{H}_2\text{O}$ .

II. 0.1240 gram substance gave 0.3120 gram  $\text{CO}_2$  and 0.0707 gram  $\text{H}_2\text{O}$ .

III. 0.1242 gram substance gave 0.3142 gram  $\text{CO}_2$  and 0.0726 gram  $\text{H}_2\text{O}$ .

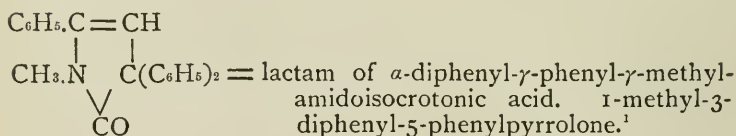
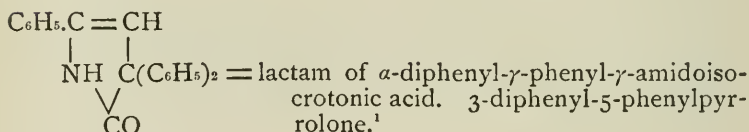
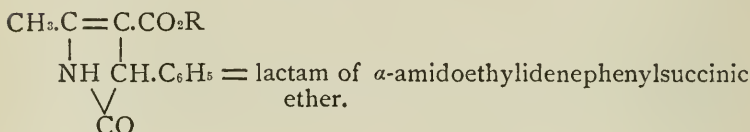
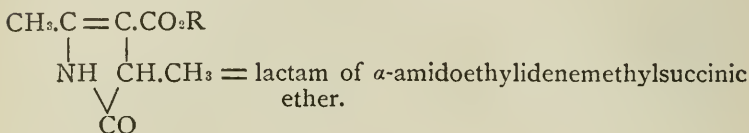
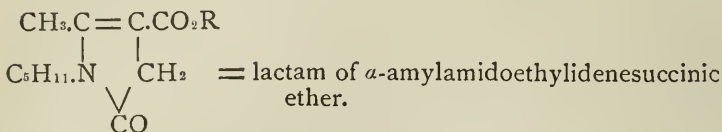
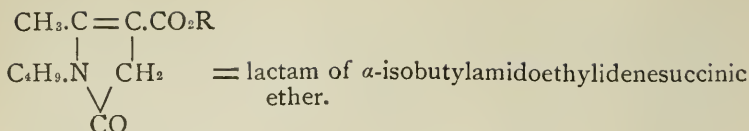
IV. 0.1710 gram substance gave the following data :  $B=745$ ,  $t=17^\circ$ ,  $v=8.6$  cc.

V. 0.2014 gram substance gave the following data :  $B=755$ ,  $t=19^\circ$ ,  $v=10.4$  cc.

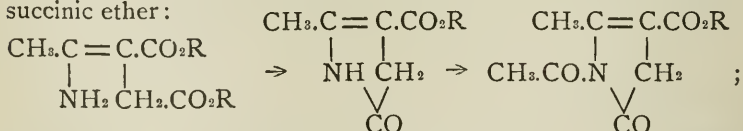
<sup>1</sup> It appears to me quite probable that Weltner (Ber. d. chem. Ges. 18, 795) has already prepared this compound, although only in small quantity. He describes the substance as crystallising in needles and melting at  $128^\circ$ – $129^\circ$ , but was unable, however, from the results of his analysis to determine its constitution.





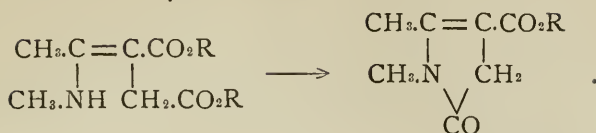


That the lactam-formula which has been exclusively employed in the foregoing is the correct one for the condensation-products arising from the action of ammonia and alkylamines on ethylic acetosuccinate is proven, first, by the formation of an acetyl derivative from the condensation-product of  $\alpha$ -amidoethylidenesuccinic ether:

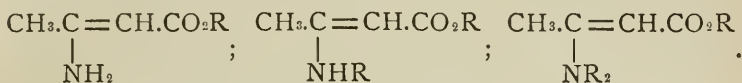


and, secondly, by the formation of the lactam of  $\alpha$ -methylamidoethylidenesuccinic ether:

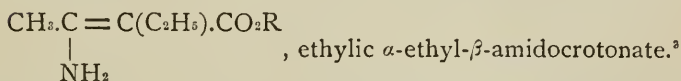
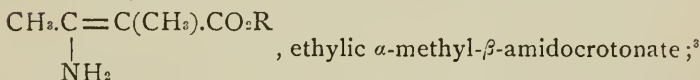
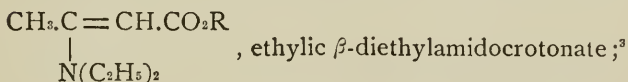
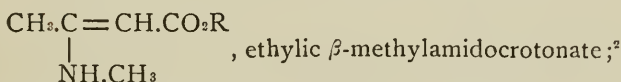
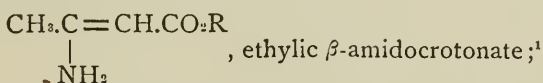
<sup>1</sup>Japp, Klingemann: Ber. d. chem. Ges. 22, 2884.



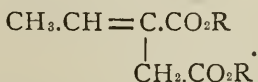
So far as the nomenclature of such ammonia- and alkylamine-derivatives of  $\beta$ - and  $\gamma$ -ketonic ethers is concerned, I believe one should be governed somewhat by the following: There can no longer be any doubt that the products formed by the action of ammonia and alkylamines on ethylic acetoacetate are constituted according to the general formulæ:



It would therefore be consistent to name them accordingly, for example, letting R represent the ethyl group —



The products formed by the action of ammonia and alkylamines on ethylic acetosuccinate may be conveniently derived from the as-yet-unknown ethylidenesuccinic ether,

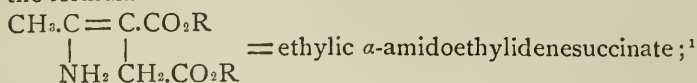


<sup>1</sup> Collie: Ann. Chem. (Liebig) **226**, 321.

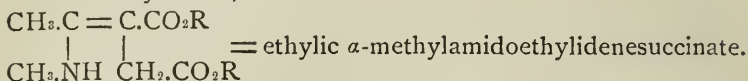
<sup>2</sup> Kuckert: Ber. d. chem. Ges. **18**, 618.

<sup>3</sup> The names given to these substances by Conrad and Epstein (Ber. d. chem. Ges. **20**, 3055) —amidomethylacetoacetic ether, amidoethylacetoacetic ether, and amidoacetosuccinic ether—appear to me to be inappropriate, inasmuch as these substances do not have the character of acetyl compounds; they do not even possess an acetyl-rest.

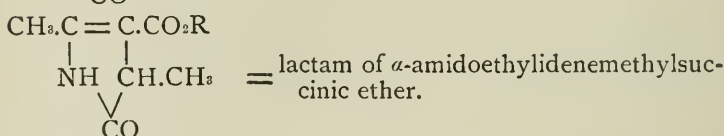
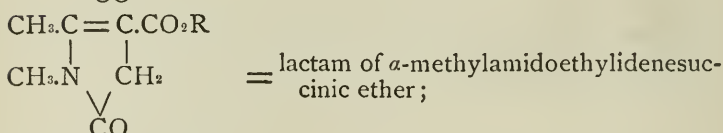
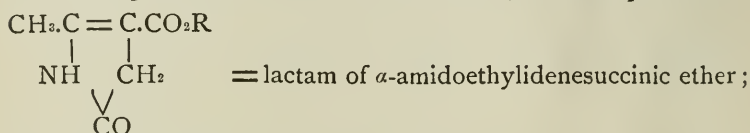
The ammonia derivative would accordingly be represented by the formula



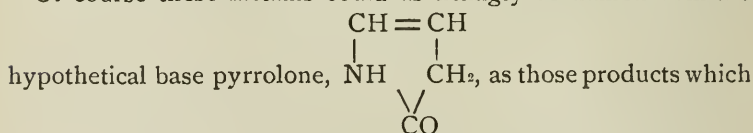
that of methylamine,



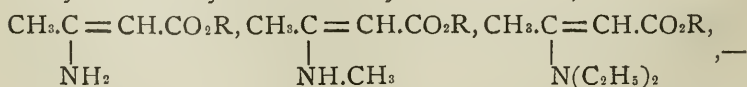
The condensation-product would simply be the lactam of that amido compound from which it was formed; for example:



Of course these lactams could as fittingly be named from the



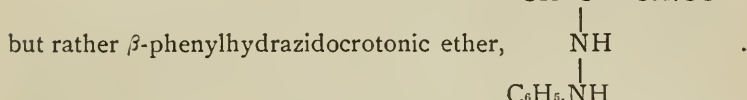
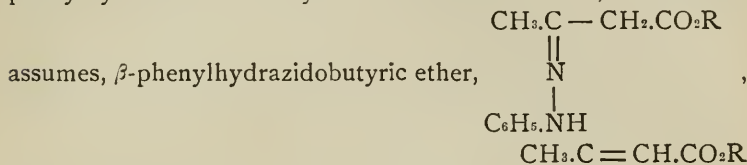
Japp and Klingemann<sup>2</sup> obtained by the action of ammonia and methylamine on  $\alpha$ - $\beta$ -dibenzoylstyrol. However, the name lactam reminds one more of the method of formation and of the general character of the substances described above; and is therefore to be preferred to the expression pyrrolone. I should here like to call attention to the fact that, if there are sufficient reasons for assuming that the products formed by the action of ammonia, methyl- and diethyl-amine on ethylic acetoacetate,—



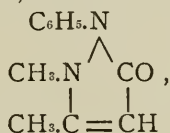
<sup>1</sup> Conrad, Epstein : Ber. d. chem. Ges. **20**, 3055.

<sup>2</sup> Ber. d. chem. Ges. **22**, 2884.

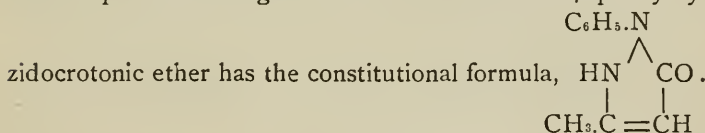
are derivatives of ethylic  $\beta$ -amidocrotonate; the same reasons justify the assumption that the substance formed by the action of phenylhydrazine on ethylic acetoacetate is not, as Knorr<sup>1</sup>



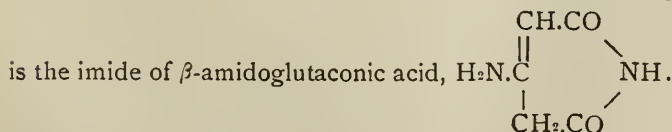
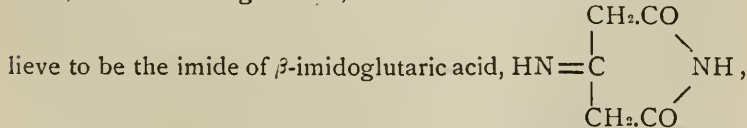
For Knorr has, by the action of symmetrical methylphenylhydrazine on ethylic acetoacetate, succeeded in preparing the same phenyldimethylpyrazolone, the so-called antipyrine,<sup>2</sup>



which is formed by the action of methyl iodide on phenylmethylpyrazolone. It is difficult to understand why symmetrical methylphenylhydrazine should act on ethylic acetoacetate in a different manner from phenylhydrazine itself. It is therefore probable that the product arising from the condensation of  $\beta$ -phenylhydra-



For similar reasons it is highly probable that the condensation-product obtained by the action of ammonia on acetonedicarboxic ether, the so-called glutazine, which Stokes and Pechmann<sup>3</sup> be-



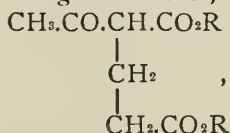
<sup>1</sup> Ann. Chem. (Liebig) **238**, 151, 160.

<sup>2</sup> Ibid. **238**, 151, 160.

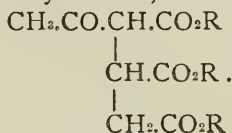
<sup>3</sup> This Journal **8**, 389.

By the action of a dialkylamine on acetonedicarbonic ether it would perhaps be possible to render an easy solution of this problem.

As a further generalisation of the reactions described above appears desirable, I have already begun a study of the action of ammonia and alkylamines on some other  $\gamma$ -ketonic ethers. I also intend to investigate the action of ammonia on a few  $\delta$ -ketonic ethers, for example,  $\alpha$ -acetoglutaric ether,



as well as  $\alpha$ -acetotricarballylic ether,



CHEMICAL LABORATORY, BONN UNIVERSITY.

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## THE SEPARATION OF TITANIUM, CHROMIUM, ALUMINUM, IRON, BARIUM AND PHOS- PHORIC ACID IN ROCK ANALYSIS.

BY THOMAS M. CHATARD.

Having to examine some magnesian silicate rocks containing, in addition to iron and aluminum, small quantities of titanium, chromium, barium and phosphoric acid, the methods for the decomposition of such rocks and the separation of their constituents were studied and compared so as to determine the most advisable manner of procedure. After repeated trials the following course, combining a number of well-known methods, has been found to be the most satisfactory.

The silica and bases are determined by the ordinary sodium carbonate fusion method, in which the hydrates of titanium, chromium, iron and aluminum, together with the phosphoric acid, are



precipitated together, and, after weighing, fused with sodium bisulphate, dissolved, the small amount of silica separated, and the solution, after reduction of the ferric oxide, titrated for total iron.

To separate these oxides and at the same time to determine the barium, two grams of the finely pulverised mineral are put into a platinum crucible or dish, moistened with water, dilute sulphuric acid (1:1) and pure strong hydrofluoric acid added in considerable excess, the vessel put on a radiator to evaporate, and stirred from time to time. When the solution is so far evaporated that fumes of sulphuric acid begin to come off, there should still be so much acid present as to form a solution or emulsion and not a paste, since the paste is liable to bake on the bottom of the vessel and form the difficultly-soluble anhydrous sulphates produced by overheating, especially when magnesia is present in quantity. At this point it is well to add a few drops of nitric acid to oxidise the ferrous oxide, and a little more hydrofluoric acid to insure the complete expulsion of the silica. The evaporation is then continued until the sulphuric acid fumes strongly and no odor of hydrofluoric acid can be detected when the solution is cooled below the point at which the sulphuric acid fumes.

About 25 cc. of dilute hydrochloric acid (1:5) is now added, the stirring being continued, and the material is then evaporated on the water-bath until most of the hydrochloric acid has been driven off. The material is then washed into a beaker, and any residue adhering to the vessel can be removed by a few drops of hot, strong hydrochloric acid, the vessel being rubbed with a bit of paper if necessary. If the solution be very turbid it can be digested on the water-bath for some time, but ultimately it is diluted with hot water to 250-300 cc., allowed to stand for several hours, and then filtered.

The residue contains the barium as sulphate, and sometimes small amounts of chromite or other minerals of the same class. It is washed, ignited and thoroughly fused with sodium carbonate in a small crucible, the fused mass being then digested with hot water and leached. The well-washed residue is dissolved on the filter with dilute hydrochloric acid, and this solution filtered through the same filter, which, after washing, is burned, the ash fused with a little sodium carbonate, the mass dissolved in dilute hydrochloric acid and added to the leachings, which are now acidified and added to the main solution, after reduction of the

chromic acid. The hydrochloric acid solution containing the barium is evaporated to a few drops to get rid of the excess of acid, diluted, the barium precipitated, and the filtrate from the barium sulphate added to the main solution.

This main solution, which should be perfectly clear and contain the iron and chromium as sesquioxides, is now made alkaline by ammonia and the precipitate redissolved by dilute hydrochloric acid. A few drops of acetic acid are added, the liquid brought to a boil, ammonia added in very slight excess, the boiling continued for a few minutes and the precipitate filtered and washed. As the sole reason for this precipitation is to get rid of the magnesia and the accumulation of other salts, the washing need not be thorough, but the filtrate must be tested and the precipitation proved complete.

The precipitate is dissolved in hot dilute hydrochloric acid. The filter after washing is burned in a large platinum crucible, into which the solution, concentrated to a small bulk, is put and evaporated on the water-bath till it becomes pasty. Just enough water is now added to dissolve the salts, and then dry sodium carbonate is added in small portions, with continual stirring, till a comparatively dry mass results. This must be carefully done, for if too much soda is added at a time, and each addition is not thoroughly stirred into the mass, the after fusion is apt to be "lumpy" and unsatisfactory.

When a good excess of carbonate has thus been added, the mass is dried and gradually brought to clear fusion, which should be continued for half an hour. If lumps form, which is, however, rarely the case if lime and magnesia are absent and the foregoing directions are followed, they can be broken up by shaking the crucible with a circular motion to detach them from its walls. When the fusion is complete, the mass is spread around the walls of the crucible and slightly cooled. A small quantity of sodium nitrate is now added, the whole rapidly fused and carefully boiled for not more than five minutes; it is then again spread over the crucible and rapidly cooled with a blast of air. The mass is boiled with water till completely disintegrated, and then leached; repeated tests have shown that the residue which contains the titanium is, when well washed, free from chromium and phosphoric acid.

The washed residue is dissolved in hot dilute hydrochloric acid, the filter burned, the ash fused with sodium bisulphate, dissolved in water and added to the solution. The titanium in this solution

is separated by the excellent method of Dr. Gooch,<sup>1</sup> all the details as laid down by him being followed. I have, however, found it convenient, after the destruction of the tartaric acid by potassium permanganate, and the clearing of the solution by sulphurous acid, to add ammonia in slight excess, then at once acetic acid in excess, and boil with addition of sulphurous acid. The precipitate of titanium hydrate, mixed with some alumina, is filtered and washed with water containing sulphurous acid and a little acetic acid. It is thus freed from manganese and brought into a small compass, rendering the after work easier. Before the final precipitation of the titanium the platinum generally in the solution should be removed by hydrogen sulphide.

The filtrate containing the chromic and phosphoric acids is heated, and ammonium nitrate cautiously added till no further precipitation of alumina occurs. The precipitation of the aluminum phosphate seems to be complete, but some alumina always remains in solution. The precipitate is allowed to settle, the supernatant liquid decanted and the precipitate washed with a solution of ammonium nitrate until the yellow tinge disappears; it is then dissolved in dilute nitric acid, and the phosphoric acid precipitated by molybdate solution.

The filtrate containing the chromic acid is acidified, boiled, neutralised with ammonia, and the chromium precipitated by freshly prepared ammoniac sulphide. The precipitate, after some washing, is dissolved in hot dilute nitric acid, and, after concentration, potassium chlorate is added, the solution boiled, and finally evaporated nearly to dryness to expel the excess of acid. It is then diluted with cold water, and a saturated solution of sodium bicarbonate added in small excess, separating the last traces of alumina. After standing about three hours, the alumina is filtered and washed with moderately dilute solution of the bicarbonate. The filtrate is acidified and the chromic acid reduced and precipitated by ammonium sulphide in a platinum dish, filtered, washed, redissolved to get rid of traces of alkali, reprecipitated, and finally weighed as chromic oxide.

This method, due to Baubigny, for the separation of aluminum from chromium is very good and convenient if the solution be free from iron and contain but little alumina. Careful tests have shown that if iron be present some of it always remains in solu-

<sup>1</sup> Proc. Am. Acad. 12, 435 seq. (Bull. No. 27, U. S. G. S., p. 16 seq.).

tion, while if there be much alumina it is almost impossible to wash out all of the chromate from the bulky precipitate with the cold solution of bicarbonate which must be used. It must also be noted in this connection that a solution of iron and chromium prepared by the Baubigny method was made ammoniacal, and it was proved that while all of the iron was precipitated, this precipitate, even after the most careful washing with hot water, contained chromium.

Although the number of details in this process may seem very great, experience has shown that none of them can safely be neglected for the purpose of shortening the work; if the whole process be carefully followed out, the results are very satisfactory, as shown by the following tests on a typical magnesian rock:

	Percentage $\text{Cr}_2\text{O}_3$ .	$\text{TiO}_2$ .	$\text{BaO}$ .	$\text{P}_2\text{O}_5$ .
No. 1,	.270	.46	.040	.375
No. 2,	.285	.39	.060	.385
No. 3,	.317	.46	.055	...
No. 4,	.280	...	...	...
Average,	.288	.44	.052	.380

The use of sodium nitrate for the fusions is not absolutely necessary, though one is more sure of complete oxidation if it be employed. In the analysis of chrome ores the best results have been obtained by fusing the finely-pulverised ore with sodium carbonate alone, but keeping it in clear fusion for an hour. The fused mass is treated like an ordinary silicate fusion, the silica after weighing being volatilised by hydrofluoric acid, and the residue, usually small, again fused with sodium carbonate, giving a clear solution in hydrochloric acid.

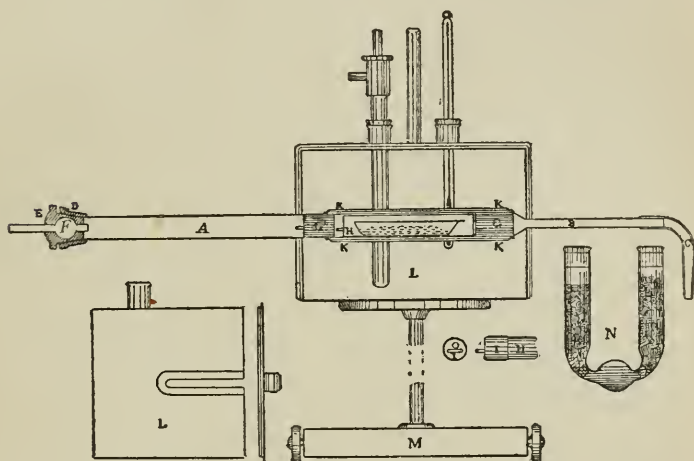
## AN APPARATUS FOR THE DETERMINATION OF WATER IN MINERAL ANALYSIS.

BY THOMAS M. CHATARD.

In all cases where the water in minerals and rocks is easily expelled, the apparatus described by me in another place<sup>1</sup> has

<sup>1</sup>Am. J. Sci. 37, 468 (Bulletin No. 60, U. S. G. S., p. 86).

been found very satisfactory. Many rocks and minerals, however, do not lose all of the water until heated for a considerable time at a temperature at which glass softens. A more refractory tube is therefore necessary, and a platinum tube, such as is used for the determination of carbon in iron and steel, has been employed to great advantage. The arrangement of the apparatus is shown in the cut.



The tube *A* has an outside diameter of 16 mm.; the small tube *B*, 5 mm. *A* need not be longer than 250–300 mm.; *B*, 80 mm. *C* is a piece of lead glass tube fused on to the end of *B* and bent and drawn out as shown. *D* is a collar of phosphor-bronze bored out with a slight taper and fitted over the end of the platinum tube, the edge of which is flanged smoothly over the face of the collar. The phosphor-bronze plug *E* has a taper corresponding to that of the collar, which it fits tightly and smoothly. The shoulders of both plug and collar are made hexagonal to insure a firm grasp when putting together or taking apart, and should be stout enough to prevent any accidental deformation. The small tube *F* is closed at the inner end, a ring of small holes being bored through the side close to the face of the plug. By this arrangement all back circulation is prevented, and the moisture which condenses in the cold part of the tube is easily and completely removed.

The platinum boat containing the substance to be examined is



placed in the cylinder *H*, made of platinum foil, which is closed at one end by a cap *I*, in the center of which is a small hole to allow the passage of the air current over the substance, while a small ring soldered to the cap permits an easy withdrawal of the cylinder. The use of this cylinder prevents a loss of any of the substance by spattering, as when sodium carbonate is mixed with it, and also the frequently resulting adhesion of the boat to the tube.

The permeability of highly-heated platinum to the gases of combustion, resulting in errors in the determination, is well known. To overcome this and also to protect the valuable tube from injury, the part where the cylinder is placed, and which is ultimately exposed to the highest heat of a blast lamp, is wrapped with several layers of asbestos paper soaked with a saturated solution of borax. The wrapping is secured with thread and dried, more borax solution being put on if deemed necessary. When quite dry, the asbestos is covered with a sheet of platinum foil *KK* secured with wire, highly heated and cooled slowly; if properly made and put on, such a wrapping should last for months of steady use, can be easily replaced when necessary, and all risk of injury to the tube is avoided.

The air-bath *L* specially constructed for this tube is a copper box, open in front with a slit at either end, as shown in *L'*, suited to the size of the two portions of the tube. The front is closed by a plate of copper, on the inner side of which several layers of asbestos board are fastened. The edges of these are slightly beveled to insure a tight fit, and a hook at the top of the bath holds the plate in place. The bath is covered with asbestos board, and, when in use, the open portions of the slits are closed by asbestos plugs. It is furnished with thermostat, thermometer and lamp, and is mounted on a stand, the base of which (*M*) is fitted with four small wheels, so that the arrangement can be pushed into position or removed without disturbing the rest of the apparatus.

When making a determination, the tube is fastened by a clamp near the end, the roll of platinum gauze *G* shoved into place, the plug inserted, and a slow stream of dry air passed through the tube, which is then heated by passing a lamp along the entire length, and allowed to cool. The boat containing the substance is now put into the cylinder, which is at once pushed into the tube till it touches the roll of gauze; the roll *G'* follows and the plug reinserted, the current of air being kept up. The air-bath, pre-



viously brought up to its standard temperature,  $105^{\circ}$ , is now opened, run into position, the tube sliding smoothly into the slits, and then closed, regaining its temperature in a few minutes. When it is considered that the tube and contents are thoroughly dry, the U-tube *N*, described in the paper already quoted, is attached, and the air-bath removed by opening it and rolling it back. The tightness of the apparatus is now tested, and, if satisfactory, the air current is regulated and the tube gradually heated, beginning at the roll *G'*, and using an ordinary burner. If much water condenses in the bent glass tube the heat must be very gradually increased, and this is best effected by keeping the part *G'* quite hot, thus heating the air current and preventing, as far as possible, the always-annoying back-circulation. Finally, the portion of the tube covered by the borax-asbestos is exposed to the full heat of a blast lamp to which a flat burner has been adapted.

When no moisture remains in the glass tube, the blast lamp is removed and the apparatus allowed to cool. When cold the U-tube is disconnected and weighed, and the cylinder with its contents withdrawn. If the amount of material at disposal is small, this portion can be used for the determination of the silica and the bases, since any loss has been prevented by the cylinder, which can be washed clean with dilute hydrochloric acid, and any insoluble matter filtered off and added to the rest of the substance in the boat, which can be fused with sodium carbonate in the usual manner.

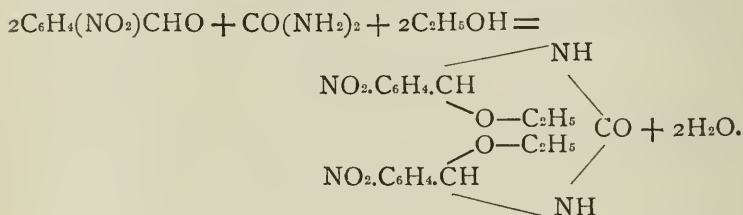
The use of the cylinder and the asbestos wrapping obviates the only serious objection to the use of this method, namely, the high cost of the platinum tube, as in this way the tube is absolutely protected from all damage. By having duplicate boats, cylinders, and U-tubes, the determinations can be made quite rapidly, and a large number of determinations made in this way by myself and others have given very satisfactory results.

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# ON BENZYLIDENEBIURET AND CHLORBENZYLIDENETHIOBIURET.

BY JOHN J. ABEL.

About a year and a half ago, Dr. Ernst Lüdy<sup>1</sup> described a method for detecting small quantities of urea, depending upon the fact that if orthonitrobenzaldehyde be added to an alcoholic solution of urea and the mixture then evaporated to dryness on the water-bath, the aldehyde combines with the urea to form nitrobenzylidenediureid, in accordance with the following equation:



An excess of either urea or orthonitrobenzaldehyde does not in any way affect the reaction, as the diureid is always formed when alcoholic solutions of these two bodies are mixed and evaporated to dryness. The resulting orthonitrobenzylidenediureid is very slightly soluble in cold or in hot water, in alcohol or in ether, and this fact condemns it as a reagent for quantitative purposes. On the other hand, the delicacy of this reaction is such that good use can be made of it in qualitative work. Thus Lüdy was able to detect urea in solutions containing less than two milligrams. For instance 0.02 cc. of an alcoholic extract containing in this volume only 0.00109 gram urea gave the diureid reaction. When the orthonitrobenzylidenediureid has formed in an alcoholic extract containing urea, the next step is to wash away an excess of either orthonitrobenzaldehyde or of urea, and then to split up the diureid with a 10 per cent. solution of sulphuric acid. The presence of the orthonitrobenzaldehyde thus set free is demonstrated by adding a little phenylhydrazine hydrochlorate, when the resulting phenylosazone at once causes the acidulated fluid to take on a beautiful deep-red color. I may remark in passing that Pickel<sup>2</sup> first showed that the three isomeric mono-

<sup>1</sup> Sitzungsber. d. kais. Akad. d. Wiss. in Wien, Bd. 98, Abth. II, b, p. 206.

<sup>2</sup> Ann. Chem. (Liebig) 232, 232.

nitrobenzaldehydes all form phenylosazones with phenylhydrazine, and Lüdy seems to have overlooked this earlier investigation.

A compound of urea easily formed and entirely insoluble in water, is still a desideratum of analytic chemistry, and the great usefulness of such a body, could it be found, in medical science especially, justifies a search for it. Therefore I gladly accepted the invitation of Prof. v. Nencki of the University of Berne to investigate the action of benzaldehyde on urea with a view to securing a product entirely insoluble in either alcohol or water. However, experiments soon showed that no insoluble condensation-product is formed in alcoholic or aqueous solutions of urea to which benzal chloride has been added. A reaction takes place only when the alcohol and water have been driven off and the point of dry heat is reached. On careful examination it was found that the resulting body is benzylidenebiuret. Now, although this body is of no use for the quantitative estimation of urea, or even for qualitative purposes, yet it was of interest more carefully to study its properties and the best way for preparing it. I obtained the best output by heating an excess of urea, say three equivalents with one equivalent of benzal chloride in a flask on the sand-bath until the thermometer registered  $198^{\circ}$  or  $200^{\circ}$  C. The beginning of the reaction is easily recognised by the appearance of gas bubbles at the boundary line between the molten urea and the benzal chloride. When the temperature has reached  $198^{\circ}$ – $200^{\circ}$  the reaction is at its height; the source of heat must now be removed and the reaction left to itself until it is complete. The contents of the flask are soon converted into a solid mass, and when this has cooled to about  $100^{\circ}$ , boiling water is poured into the flask, and the granular mass is well stirred and the solution filtered. The white mass remaining in the flask and on the filter is treated several times with hot alcohol and decanted. The substance now remaining is largely freed from the by-products of the reaction and must be dissolved in hot water, very large quantities of which are necessary. Out of this aqueous solution large, glistening rhombic prisms crystallise when the conditions are favorable to a slow crystallisation; otherwise clusters of fine needles are formed. The aqueous and alcoholic solutions filtered from the crude product also yield these crystals, mingled, however, with much ammonium chloride.

The empirical formula of benzylidenebiuret as determined by

analysis of the large rhombic crystals, several times recrystallised, and by molecular-weight determinations according to Raoult's method, is  $C_9H_9N_3O_2$ . Inasmuch as ammonium chloride and cyanic acid are the only by-products of the reaction, it may be expressed in the terms of the following equation:



Combustion analyses of the large crystals, twice crystallised and dried at  $110^\circ$  C. until of constant weight, gave the following results:

I. 0.2898 gram substance gave 0.6 gram  $CO_2$  and 0.1372 gram  $H_2O$ .

II. 0.2463 gram substance gave 0.5085 gram  $CO_2$  and 0.1087 gram  $H_2O$ .

III. 0.248 gram substance gave 51 cc. N at  $16^\circ$  C. and 711 mm. pressure = 0.0555 gram N; or, by percentage,—

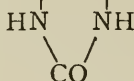
	I.	II.	III.	Required for $C_9H_9N_3O_2$ .
C	56.77	56.30	...	56.54
H	5.26	4.90	...	4.71
N	...	...	22.39	21.98

As the body is sufficiently soluble in phenol, molecular-weight determinations according to Raoult's method were made in the manner already described by me.<sup>1</sup> 0.3204 gram substance was dissolved in 12.737 grams phenol, and the freezing point was found to be lowered by  $0.96^\circ$ . The molecular weight of the body therefore, determined according to Raoult's formula,  $M = \frac{T.P.100}{D.L.}$ , is 199. In a second experiment, 0.4434 gram substance was dissolved in 21.022 grams phenol, and the resulting depression of the freezing point amounted to  $0.78^\circ$ , and  $M$  was found to be 205. The empirical formula  $C_9H_9N_3O_2$  demands for  $M$  191. The melting point of the body lies at  $258^\circ$  C., uncorrected, and at this temperature decomposition occurs.

Whether the benzylidene substitutes two hydrogen atoms in the same amidogen group and the resulting biuret is to be represented by the formula  $C_6H_5-CH=N-CO-NH-CO-NH_2$ , or whether the substitution occurs in the manner indicated by the

<sup>1</sup> Sitzungsber. d. kais. Akad. d. Wiss. in Wien. 99, Abth. II, 79-80.

following closed formula,  $\text{C}_6\text{H}_5\cdot\text{CH} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$ , is not easily decided.



Of the two structural formulæ, the latter is probably the correct one, for the body is not more soluble in dilute mineral acids than in water, and this speaks against the presence of an amidogen group. On the other hand, I was not able to get a nitrosamine by treating the body with potassium nitrite or amyl nitrite.

Aqueous solutions of benzylidenebiuret are precipitated by most metallic salts. Thus, mercuric chloride gives a precipitate consisting of white granules, which, examined under the microscope, are seen to be aggregates of small, pointed crystals. The chloroplatinate obtained by precipitating an aqueous solution with a 5-per cent. solution of platinum chloride, crystallises in thin plates of rhombic form. Chloride of iron yields a double salt, which crystallises in thin, glistening plates.

With regard to the solubility of the body, I may say that it is partially soluble in phenol, in hot water, and in alcohol; very slightly, or not at all, in ether and chloroform, and insoluble in carbon bisulphide.

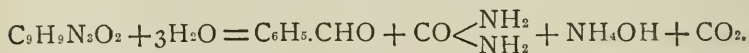
In order to study the action of hydrolytic agents upon benzylidenebiuret, I treated it with dilute sodium hydroxide, and also with barium hydroxide. When boiled with a dilute solution of the former, ammonia is evolved and the odor of benzaldehyde is noticed. In order to study the decomposition products resulting from treatment with caustic alkalis, I proceeded as follows:

60 grams of barium hydroxide were dissolved in 400 grams of hot water, filtered, and poured upon 4 grams of the substance previously put into a liter flask to which a reflux condenser was attached, and the whole kept at a boiling heat on the sand-bath for four hours, after which the white sediment which had formed was filtered off while hot.

During the boiling the odor of benzaldehyde is very marked, and a piece of moistened litmus paper held in the current of escaping steam is turned blue. The filtrate was kept warm on the water-bath and carbon dioxide passed through it until a test-filtrate showed that it was fairly free from barium precipitable by



a current of carbon dioxide. It was then set aside for ten hours and again heated on the water-bath, while carbon dioxide was again passed through until all the barium removable in this way was precipitated. The clear filtrate was now evaporated to dryness on the water-bath, the residue dissolved in a very little water and treated with hydrochloric acid. The crystalline precipitate thus produced was several times recrystallised out of hot water, and when sufficiently purified was, through a study of its melting point, crystalline form and capability of sublimation, proved to consist of benzoic acid. The fluid remaining after precipitating the benzoic acid with hydrochloric acid, was evaporated on the water-bath and treated with alcohol. By Lüdy's method the presence of urea in the alcoholic extract was easily shown. But the urea was also isolated and its identity established by its crystalline form, by the characteristic crystals of its nitrate, and by the fact of its giving the biuret reaction and yielding ammonia when treated with hot sodium hydroxide. Therefore boiling this body with barium hydroxide causes it to split up, while taking up water, according to the following equation:



I will add that, if it be dissolved in concentrated sulphuric acid and then diluted with water, a compound crystallises out in large clusters of rhombic prisms.

Inasmuch as urea and benzal chloride yield benzylidenebiuret, it was of interest to see if benzal chloride and sulpho-urea would yield the corresponding sulpho-biuret, especially as this body was made by L. Brodsky<sup>1</sup> some years ago in a very different manner, viz., by heating together benzaldehyde and ammonium sulphonyanate. Benzal chloride heated with sulpho-urea reacts violently, the temperature rises rapidly and there is a lively evolution of gas bubbles, the contents of the flask taking on first a yellow, and then a brownish color, and, unless benzal chloride is present in great excess, only a reddish resinous mass is left. After numerous experiments I found the following to be the best method for obtaining a tolerably pure product:

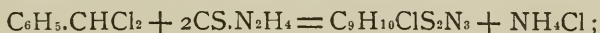
40 grams of dry sulpho-urea and 60 grams of benzal chloride are heated in a flask on a paraffin-bath until the beginning of a

<sup>1</sup> Sitzungsber. der kais. Akad. der Wiss. in Wien. 95, II Abth. 69.



reaction is observed. At 150° C. the reaction is already so violent that the flask must at once be removed from the bath in order to keep its contents from turning into a resinous by-product. If an excess of benzal chloride has not been taken, and if the temperature has not been watched with the greatest care, it will rise rapidly to 190° C. in spite of the removal of the flask from the paraffin-bath. Reddish-brown vapors, extremely irritating to the mucous membrane, arise in clouds, and, when these cease to be given off, only the unutilisable resin before spoken of remains. On the other hand, when a sufficient quantity of benzal chloride has been taken and the temperature has not been allowed to go above 150° C., a reddish-yellow granular mass is formed, the development of gas is only moderate, and colored vapors do not appear. After cooling, the raw product is recrystallised out of hot water, in which, however, it dissolves with difficulty, and for its complete purification the product thus obtained is several times precipitated from hot alcohol by ether, which causes it to fall in snow-white crystalline flakes. These when dried over sulphuric acid gave on elementary analysis results which correspond with the empirical formula  $C_9H_{10}ClN_2S_3$ . Determinations of the molecular weight also gave results which speak for this formula. Thus  $M$  was found to be 251; calculated, 259.

Accordingly we may perhaps regard this body as being formed in agreement with the following equation:



and as being chlorbenzylidenethiobiuret. At any rate the benzylidenebiuret of Brodsky is not formed in this reaction. In addition to chlorbenzylidenethiobiuret and ammonium chloride no other bodies were obtained. It is my purpose to determine the constitution of chlorbenzylidenebiuret by repeated analyses of its salts and of its decomposition-products. I may add that by dissolving it in concentrated sulphuric acid or in glacial acetic acid, new and beautifully crystalline chlorine-free products are obtained.

## HYDRATED LEAD OXIDE.

BY C. LUEDEKING.

There seem to be at least two hydrated oxides of lead;  $3\text{PbO} \cdot \text{H}_2\text{O}$  obtained by Payen,<sup>1</sup> and  $2\text{PbO} \cdot \text{H}_2\text{O}$  prepared by Schaffner.<sup>2</sup> Payen obtained his hydrate in the form of strongly-refracting octahedra by allowing an ammoniacal solution of lead acetate to crystallise in a closed vessel. It is very questionable whether the crystals so obtained are entirely free from basic salt or ammonia. Calvert<sup>3</sup> observed that hydrated oxide of lead can combine with ammonia, and Winkelblech<sup>4</sup> maintains that the hydrated oxide so obtained always contains small amounts of basic salt which cannot be removed by excess of alkali.

Schaffner claims to be able to obtain his hydrated oxide entirely free from basic salt by precipitating a solution of lead acetate with a slight excess of potassium hydrate.

It is possible to obtain the hydrated oxide of lead of Schaffner in excellent crystals in another way, which may form the basis for obtaining from other metals also hydrated oxides soluble in potassium hydrate. When litharge is boiled with a strong solution of potassium hydrate for some time, a considerable amount of it passes into solution. The potassium hydrate solution, when strong, deposits on cooling a large quantity of crystals of anhydrous protoxide of lead, as had been observed by several authors previously. The solution, after it has become perfectly cold, however, still contains a large amount of lead oxide. When now it is exposed in a small beaker to the air, carbon dioxide is slowly absorbed and potassium carbonate formed. Thus the lead is gradually and very slowly deprived of its solvent and all conditions for crystallisation pertain. After several weeks the bottom of the vessel will be found covered with magnificently-developed crystals, perfectly colorless and transparent, and having a high refractive-power for light and brilliant luster. These crystals, on examination, are found to be the hydrate  $2\text{PbO} \cdot \text{H}_2\text{O}$  in a state of absolute purity. They belong to the tetragonal system, are simple in development and short and thick in habit, showing the prism  $\infty P \infty$ , and the pyramid  $P$  at either end. The angle between

<sup>1</sup>Ann. chim. phys. [4] 8, 302.<sup>2</sup>Compt. rend. 22, 480.<sup>3</sup>Ann. Chem. (Liebig) 51, 175.<sup>4</sup>Ann. Chem. (Liebig) 21, 29.

the opposite edges, over the solid angle of the pyramid, is  $101^\circ$ . The axial relations are  $1 : 1 : 0.824$ . Their reaction is alkaline, and on exposure to the air they soon become opaque, absorbing carbon dioxide and forming lead carbonate. In this metamorphosis, however, they maintain sharply their original form. On heating they lose their water and become yellow litharge, but nevertheless maintain the original crystalline form.

The structure of this hydrate is probably the following:  $\begin{array}{c} \text{Pb} < \text{OH} \\ < \text{O} \\ \text{Pb} < \text{OH} \end{array}$ .

We may consider that it is rather to be expected that the weaker the base the fewer OH-radicals will it contain. Take, for example, calcium hydrate—a much stronger base—and we have all the affinities of calcium saturated with hydroxyl groups.

The less the basic powers of an element, when it can form hydrates, the greater the likelihood of its forming such hydrates as that we have examined, and even others such as  $3\text{PbO} \cdot \text{H}_2\text{O}$ , which has, in fact, been actually obtained. Thus it will be easy to form from a strong base a hydrated oxide containing the normal number of hydroxyl groups, while for a weak base this will be difficult; and *vice versa*. This will explain in a chemical way what appears at first anomalous and only mechanical admixture, viz., the small amount of water contained in many oxides of the heavier metals.

CHEMICAL LABORATORY, WASHINGTON UNIVERSITY.

## ON THE MELTING POINT OF CERTAIN ALLOYS.

BY FRED. C. WELD.

In some experiments which I made for practical purposes I had occasion to determine the melting points of several low-melting alloys. In view of the work of Heycock and Neville, it seems worth while to publish the results.

Heycock and Neville<sup>1</sup> find that each atom of the following metals alloyed with 100 atoms of tin reduces the melting point—

<sup>1</sup> Chem. News 59, 175.

or, in the case of antimony, raises it—as follows: zinc,  $2.53^{\circ}$ ; copper,  $2.47^{\circ}$ ; silver,  $2.67^{\circ}$ ; cadmium,  $2.16^{\circ}$ ; lead,  $2.22^{\circ}$ ; mercury,  $2.3^{\circ}$ ; aluminium,  $1.34^{\circ}$ ; antimony,  $2^{\circ}$ .

My results show the limit to which this is true in the case of tin and lead:

Melting point of tin (fine bar).		Atoms of lead,		Factor for lead.		Calculated melting point.	Found.
$227^{\circ}$	minus	3.28	×	$2.22^{\circ}$	=	$219.72^{\circ}$	$218^{\circ}-219^{\circ}$
"	"	11.24	×	$2.22^{\circ}$	=	$202.05^{\circ}$	$201.5^{\circ}$
"	"	15.13	×	$2.22^{\circ}$	=	$193.41^{\circ}$	$194^{\circ}$
"	"	17.19	×	$2.22^{\circ}$	=	$188.84^{\circ}$	$193^{\circ}$
"	"	19.47	×	$2.22^{\circ}$	=	$183.78^{\circ}$	$188^{\circ}-190^{\circ}$
"	"	38.18	×	$2.22^{\circ}$	=	$142.24^{\circ}$	$180^{\circ}$
"	"	57.28	×	$2.22^{\circ}$	=	$99.84^{\circ}$	$180^{\circ}$
"	"	85.12	×	$2.22^{\circ}$	=	$38.03^{\circ}$	$209^{\circ}$

It will be seen from these figures that the rule of Heycock and Neville holds only to 15 atoms of lead in 100 of tin; further, that the lowest melting point possible is obtained from 38 atoms of lead. I am not prepared as yet to advance any theory to account for these phenomena.

The method used was very simple, but gave satisfactory results. The alloys, after being fused and cooled, were again fused and stirred while cooling with an ordinary glass thermometer. Melting points obtained in this manner checked exactly with one made in an ordinary melting-point apparatus. My lower results check within a degree those of Heycock and Neville, and the melting point of the tin is within a degree of that of pure tin ( $228^{\circ}$ ).

The effects of this reduction of the melting point are not cumulative, *e. g.*, the melting point of an alloy of 100 atoms of tin and 57.28 atoms of lead is  $180^{\circ}$ ; the melting point of an alloy of 100 atoms of tin, 57.28 atoms of lead and 5.89 atoms of mercury is not  $180^{\circ} - 5.89 \times 2.3^{\circ} = 166.45^{\circ}$ , but is  $173^{\circ}$ . So also the calculated melting point for an alloy of 100 atoms of tin, 57.28 atoms of lead and 19.2 atoms of mercury would be  $131.23^{\circ}$ ; the actual melting point is  $156^{\circ}$ .

The following alloys containing bismuth, for which as yet no factor has been determined, were tested. In the calculated melting point the bismuth has been left entirely out of consideration, although it undoubtedly reduces the melting point. The starting point in the calculation has been  $180^{\circ}$ , the melting point of an alloy of 57.28 atoms of lead and 100 atoms of tin.

Tin (atoms).	Lead (atoms).	Mercury (atoms).	Zinc (atoms).	Bismuth (atoms).	Calculated.	Found.
100	57.28	12.58	7.04	3.3	133.26°	145°-150°
100	57.28	8.41	...	2.24	160.66°	166°-167°
100	57.28	10.58	13.02	4.03	122.72°	148°
100	57.28	12.82	5.63	2.66	136.27°	145°

## THE DETECTION OF CONIINE IN A CASE OF POISONING.

BY LAUNCELOT W. ANDREWS.

Coniine so rarely takes a part in toxicological cases that a brief report of such a case will perhaps possess sufficient interest to warrant publication, more especially since the investigations of recent years concerning ptomaines have so greatly complicated the labors of the toxicologist and increased the chances of escape of the criminal by enabling him to ascribe the observed reactions of an isolated poison to some hypothetical ptomaine. So long as our knowledge of this latter class of bodies is confessedly incomplete, the expert may be confronted with the question, "How do you know that no ptomaine exists which may give all the reactions of the alkaloid you profess to have discovered?" and he will find it a hard one to answer in such a way as to satisfy an average jury.

In the particular case which forms the motive of this article I succeeded in determining the molecular weight of the alkaloid found (coniine) through the analysis of one of its salts, and thus characterised it more positively than would be possible by means of qualitative reactions alone. The demonstration of the feasibility of this method has not, so far as I am aware, previously been offered. I cannot but believe that it is capable of more extended application.<sup>1</sup>

The objects submitted to me for examination in the case of the State of Iowa *v.* V. de V., with instructions to "look for strychnine

<sup>1</sup> I do not wish to be understood as saying by this that the amount of substance available would always or even usually be sufficient for a molecular-weight determination, but would emphasise the importance of such a determination when possible.



nine and other poisons," consisted of a jar of soup and a stomach. The latter was, remarkably enough, immersed in a jar of a preservative sold under the name of "bromo-chloralum," which consists mainly of a solution of the chlorides of magnesium and aluminum with a small quantity of bromides.

The ligatures at the ends of the stomach were so indifferently secured that one of them had come off, allowing the contents of the stomach to mix with the preservative solution. The comparatively large quantity of aluminum and magnesium salts soluble in alcohol thus brought of necessity into the analysis was of course troublesome in the examination for alkaloids. The interior of the stomach was coated with a coffee-colored scum or fur. It exhibited near the pyloric end some large inflamed patches and numerous small pin-head dots of intense inflammation. Inspection with a magnifier failed to reveal any foreign substance in connection with these spots.

The examination for inorganic poisons may be passed over, since it revealed nothing abnormal beyond the constituents of the "bromo-chloralum" above mentioned.

In the examination for alkaloids the method of Dragendorff was in the main followed. The stomach (and contents, see above) was examined in several portions.

162 grams cut up fine were digested for some time with pure 96 per cent. alcohol and ten drops of sulphuric acid. The liquid was strained off, the residue washed with alcohol, and filtrate together with washings evaporated at 50° C. to one-third its former bulk.

This solution when cold was strained, filtered and shaken successively with petroleum ether,<sup>1</sup> benzene and chloroform. Each of these solvents after washing with water left upon evaporation amorphous residues, not bitter and not possessing alkaloidal properties. A marked tendency to form emulsions was met by repeated filtrations through absorbent cotton.

The solution was then rendered alkaline with sodium hydrate and filtered.<sup>2</sup> The precipitate was washed with a little alcohol, and a portion of the filtrate together with washings shaken with petroleum ether. The petroleum ether solution after filtration was allowed to evaporate on a watch-glass with a drop of concen-

<sup>1</sup> Previously purified by shaking with concentrated sulphuric acid and by fractional distillation.

<sup>2</sup> The filtrate is designated "B."



trated hydrochloric acid. This turned red and then violet blue.<sup>1</sup> The hydrochloric acid on evaporation left a crystalline residue (needle and dagger forms, etc.), contaminated with dark colored amorphous matter. For further purification it was treated with absolute alcohol, filtered and evaporated. This residue was colorless and crystallised in needles.

With this substance the following reactions were obtained: With phosphomolybdic acid, pale yellow amorphous precipitate. With potassio-mercuric iodide, the same. With mercuric iodide, white amorphous precipitate. With gold chloride, pale yellow micro-crystalline precipitate. With concentrated sulphuric acid and potassium dichromate, no coloration except from gradual reduction of chromic acid. With picric acid, no change.<sup>2</sup> With platinic chloride, no change. With potassium bichromate, no precipitate. With iodine in potassium iodide solution, brown precipitate, which disappears and is reproduced upon further addition of the reagent.

The rest of the solution mentioned above and designated "B" was then in part shaken with chloroform, in part with ether ("C"). From the former was obtained with hydrochloric acid a mass of trabecular crystals indistinguishable from coniine hydrochloride, of which a specimen for direct comparison was prepared by recrystallisation under similar conditions from a sample of Merck's.

This preparation exhibited under the polarising microscope the well-known play of colors. It weighed 1.0 milligram, and was utilised for a physiological test.\* For this purpose it was dissolved in a small quantity of water and administered hypodermically to a cat. Great dilation of the pupils ensued, and they did not contract when exposed to the light of a burning magnesium ribbon. The animal's nose turned blue, violent trembling followed and continued for a long time. The respiration became labored and irregular, the hind legs weak or partially paralysed, then a nearly-complete torpor set in, followed by recovery in four hours.

<sup>1</sup> Reaction of imperfectly purified coniine. (Dragendorff: "Gerichtlich-chemische Ermittlung von Giften," 2d ed., p. 243.)

<sup>2</sup> Ibid. p. 132. Wormley states that an alcoholic solution of picric acid precipitates coniine from "aqueous solutions," an observation which I cannot confirm. The drawing which he gives of crystals of coniine picrate bears a remarkably close resemblance to crystals of picric acid such as may be obtained by adding an alcoholic solution of picric acid to water. (Vide *Micro-chemistry of Poisons*, page 451 and plates.)

The ether solution ("C") evolved a distinct odor of coniine. On treatment with hydrochloric acid and evaporation it left a crystalline residue identical with that already described, and which with a drop of sodium hydrate solution emitted an intense coniine odor, microscopic oily globules forming in the drop at the same time. This hydrochloride, in addition to the reactions obtained with the previous preparations, on solution in water and treatment with a solution of bromine in hydrobromic acid, gave a magma of felted crystals intermingled with orange oily droplets.

A further portion of the stomach, etc., weighing 135 grams was worked up with an especial view to isolating, if possible, a sufficient quantity of the alkaloidal hydrochloride above described for a quantitative determination of the hydrochloric acid. The material was digested with its own weight of alcohol and ten drops of sulphuric acid for ten hours, then strained and the residue exhausted with alcohol. The united solutions, after distillation to one-third of original volume, were strained, filtered and evaporated at a low temperature under reduced pressure to the consistency of a viscid syrup. This was thoroughly mixed with about six volumes of absolute alcohol, filtered, evaporated as before to a thick syrup, dissolved in a small quantity of water and filtered. This liquid was washed by shaking once with chloroform. Then it was made alkaline with sodium carbonate and shaken with chloroform. The whole mass became at this point a pasty emulsion smelling of coniine. It was stirred up with some freshly ignited asbestos fiber and filtered with the aid of a vacuum pump, the precipitate being washed with a few drops of absolute alcohol and chloroform. The filtrate was carefully treated with a slight excess of sodium hydrate, which produced a fresh precipitate (consisting of magnesium hydrate). It was again shaken with the same chloroform and again filtered. The chloroform now separated readily from the aqueous layer.

The latter was exhausted of alkaloid by successive shakings with small quantities of chloroform. These chloroform solutions were one by one well shaken with about 10 cc. of normal hydrochloric acid until the test with iodine solution showed that they had parted with all their alkaloid. The colorless hydrochloric acid solution was made alkaline with sodium hydrate, and twice shaken with three times its volume of chloroform. The latter was drawn off, filtered clear, and exposed *in vacuo* over sulphuric acid

until its volume was reduced to about 15 cc. (removal of ammonia). It was then treated with hydrochloric acid gas, which caused turbidity and the separation of colorless acicular crystals. It was then allowed to evaporate *in vacuo* in contact with two drops of concentrated hydrochloric acid. The crystalline residuum exhibited crystals of two kinds, viz. ammonium chloride and coniine hydrochloride. On treatment with absolute alcohol the latter dissolved. The filtered alcoholic solution, after evaporation, left a trabecular mass of crystals showing a superb play of colors when examined in polarised light. Crystals of ammonium chloride could not be detected with the polarising microscope in this preparation, which appeared entirely homogeneous.

The weight of the crystals was .0102 gram. They were dissolved in water, and the hydrochloric acid in them titrated by Mohr's method with  $\frac{3}{100}$  normal silver nitrate. The burette employed was of very narrow caliber and divided into  $\frac{1}{50}$  cc., being easily read to  $\frac{1}{100}$  cc.

Required 2.10 cc.  $\frac{3}{100}$  normal silver nitrate solution = 2.293 milligrams HCl found = 22.48 per cent. HCl.

Calculated for coniine hydrochloride,  $C_8H_{17}NHCl$ , 22.28 per cent.

Molecular weight of base, found, 125.4.

Molecular weight of coniine, calculated, 126.8.

It will be unnecessary to describe in detail the detection of coniine in the soup of which the deceased had partaken four hours before her death. The methods employed were essentially the same as those already described, and the results were identical, except that the observed reactions indicated the presence of a relatively much larger amount of coniine, which was unmistakably identified by all its reactions specified above, and by the well known characteristic behavior of its saturated aqueous solution when alternately warmed and cooled.<sup>1</sup>

All the solvents used in this investigation were run through parallel blank tests, which established their purity as regards substances of alkaloidal reaction.

It is with confidence that I submit to the judgment of the profession at large the claim made by the defense that the alkaloid isolated by me and identified as coniine was in reality an unnamed ptomaine.

<sup>1</sup> Beilstein; *Organische Chemie*, 2nd Ed., 3, 627.

This assertion will be estimated at its true value when it is remembered, in addition to the direct evidence, that the stomach and the soup had been subjected to entirely different conditions, that they constituted perfectly distinct "nutrient media." Under these circumstances the unsupported assumption that in both objects precisely the same ptomaine should have been generated lacks rational basis.

CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.

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## THE DISSOCIATION OF MAGNESIUM OXIDE BY MEANS OF METALLIC MAGNESIUM.

BY H. N. MORSE AND J. WHITE, JR.

In former papers<sup>1</sup> we have described the dissociation which takes place when the oxides or sulphides of zinc and cadmium are heated in a vacuum with their respective metals. Since then we have found that the oxide of magnesium undergoes an equally unmistakable dissociation when it is heated in the same way with metallic magnesium.

The apparatus which we employed was essentially the same as that used in the dissociation of the oxides and sulphides of zinc and cadmium, except that, owing to the energetic action of the vapors of magnesium on silicates, it was found advantageous to inclose the mixture of oxide and metal in a tube of sheet-iron. The iron tube was made by forming a thoroughly-cleansed strip of the metal, from 40 to 45 centimeters long, around an iron rod of proper thickness, and closing one end with the hammer. It was then prepared for use by inclosing it in a glass tube, exhausting with the Sprengel pump, and heating to redness until it ceased to give off volatile matter.

Owing to the presence of considerable quantities of occluded hydrogen in commercial magnesium, as observed by Dumas,<sup>2</sup> the metal was distilled in a vacuum in the manner described by Burton and Vorce.<sup>3</sup> The oxide of magnesium, also, was heated to redness in a vacuum until it ceased to give off carbon dioxide.

<sup>1</sup> This Journal 11, 258 and 348.

<sup>2</sup> Compt. rend. 90, 1027.

<sup>3</sup> This Journal 12, 219.

The metal and then the oxide were dropped into the iron tube. This was then placed in a larger tube of hard glass which had been closed at one end. The length of the glass tube was usually about 80 centimeters, or twice that of the iron tube. The outer tube was then drawn out at the open end, attached to the Sprengel pump, exhausted, and finally heated in a combustion furnace along that portion which was occupied by the iron tube. The quantities of magnesium employed in our experiments varied from 4.5 to 10 grams; those of the oxide, from 1.5 to 3 grams.

In every case the phenomena which presented themselves when the tube had reached a bright red heat were similar to those observed when the oxides of zinc and cadmium were heated with their metals. The oxide formed in the cool portion of the glass tube, and fell upon the bottom in a long line which extended even into the connecting tube of the pump itself. This transportation of the oxide continued until the greater portion of the metal had distilled to and condensed about the open end of the iron tube. At the same time gas was evolved and collected in the eudiometer placed over the outlet of the pump. This gas proved to be a mixture of carbon dioxide and free oxygen. The proportion of the oxide thus transported to the cooler portion of the glass tube was quite variable, and appeared to depend on the thoroughness with which the oxide and metal were mingled in the iron tube. It was always found to be greater when the mixture of oxide and metal which remained in the inner tube after one experiment was reheated with an additional quantity of magnesium. It was not possible to determine the exact amount of oxide which was carried out of the iron tube, owing to the presence in it of some distilled metal; but on several occasions that portion of the oxide which was nearest the pump and appeared to be free from metal was collected and weighed. The quantity varied from 0.1 gram to 1.5 gram. In some cases only a small fraction of the oxide remained in the iron tube.

As in the case of the oxides of zinc and cadmium, the evolution of oxygen was most rapid during early stages of the experiment, before the tube had become filled with the vapors of the metal. The carbon dioxide, which must have come from the carbon contained in the iron, was removed by caustic potash, and the oxygen determined by means of an alkaline solution of pyrogallie acid. The quantity of oxygen found varied from 1.5 to 3 cc.



ANALYSIS OF MILK OF RIPE AND UNRIPE  
COCOANUTS.

BY LUCIUS L. VAN SLYKE.

As a member of the U. S. Yellow Fever Commission, Dr. Geo. M. Sternberg, during a residence in Cuba for the purpose of investigating the yellow fever, made use of the milk of unripe cocoanuts as a culture medium for studying certain bacteria. In order to ascertain the composition of the milk so used, Dr. Sternberg procured six unripe cocoanuts from Cuba and placed them in my hands for analysis.

What is known as the meat of the cocoanut had in each of these six nuts just begun to form, covering the inside of the shell with a very thin, soft, nearly transparent layer.

So far as I have been able to ascertain, there is not on record any analysis of the milk of the cocoanut at this stage of growth. Hammerbacher has published an analysis of the mixed milk of two cocoanuts, which were presumably ripe, like those ordinarily obtained in the market. For purpose of comparison, I also made an analysis of the milk of one ripe cocoanut.

The milk of the unripe nuts was transparent like water, containing in suspension small amounts of a cloudy-white substance which was readily removed by filtration. In the ripe nut, the milk was quite turbid in appearance and did not filter clear.

Following is a brief explanation of the methods employed in making some of the determinations:

1. A picnometer was used for determining specific gravity, careful attention being given to temperature.
2. The water was determined by heating a weighed portion at 60° C. to constant weight. A temperature much above this causes dehydration of the glucose and a correspondingly increased percentage of water.
3. In determining the amount of albuminoids, about 60 grams of milk were evaporated to a small bulk and the nitrogen determined according to the Kjeldahl process as modified by Gunning. The amount of nitrogen thus obtained was multiplied by the factor 6.25 to determine the amount of albuminoids.

The following table gives the results of the different analyses, including those of Hammerbacher's analysis:



ANALYSIS OF MILK OF COCOANUTS.	MILK OF UNRIPE COCOANUTS.						Milk of Ripe Cocanut.	Hammerbacher's Analysis.
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Weight, in grams	230.5	378.6	347.	383.7	350.	330.	109 6	151.9
Specific Gravity, at 15.5° C.	1.0246	1.023	1.0223	1.023	1.0221	1.0215	1.044	1.0442
Water, per cent., at 60° C.	94.37	94.48	94.59	94.89	95.27	96.43	91.23	91.50
Ash, per cent.	0.575	0.635	0.675	0.611	0.608	0.602	1.06	1.19
Glucose, per cent.	4.58	3.83	3.45	4.06	4.36	3.56	Trace	....
Cane Sugar, per cent.	Trace	Trace	Trace	Trace	Trace	Trace	4.42	....
Albuminoids, per cent.	0.120	0.126	0.114	0.205	0.140	0.095	0.291	0.46
Fat, per ct. (Ether extract)	0.084	0.100	0.138	0.131	0.145	0.120	0.145	0.07

Briefly comparing the results given in the foregoing table, we notice that the milk of the ripe cocconut differs from that of the unripe cocconut in the following particulars:

The former is, first, less in amount in each nut; second, greater in specific gravity; third, contains less water; fourth, contains more ash and albuminoids; and fifth, contains cane sugar with traces of glucose, the opposite being true in case of the milk of the unripe nut, which contains glucose with traces of cane sugar.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

## REVIEWS AND REPORTS.

### RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

#### III.—*Chlorates, Electrolysis, and Potassium Salts.*

*Chlorates.*—The ordinary process for the manufacture of potassium chlorate consists, as is well known, in passing chlorine into milk of lime, forming a solution of calcium chlorate and chloride, then decomposing the chlorate by the addition of an equivalent

quantity of potassium chloride, and crystallising out the potassium chlorate formed. Theoretically, the action of chlorine on lime should give five equivalents of chloride to one of chlorate; practically, nearly six equivalents of chloride are obtained. It is impossible to separate the potassium chlorate completely from the large amount of calcium chloride by crystallisation, and under ordinary circumstances about twenty per cent. of the product is lost in the mother-liquors. Hammill<sup>1</sup> finds that this loss can be greatly reduced by diluting the liquor slightly and lowering its temperature to 0° C. by refrigerating apparatus. By this method the yield of chlorate is said to be increased one-seventh, and the loss is reduced to nine or ten per cent.

A further modification of the old method is the process of Muspratt and Eschellmann, in which magnesia instead of lime is suspended in water and saturated with chlorine. Magnesium chloride and chlorate are produced in about the same proportion as the corresponding calcium compounds; by evaporation, however, one-half the magnesium chloride may be crystallised out, thus making it possible, after the addition of the potassium chloride, to separate the chlorate far more completely than in the ordinary process. The magnesium chloride obtained in large quantity as a by-product is sold for use in the sizing of cotton. This method is in use at the works of James Muspratt & Sons, Widnes, England.

The process of the future for the manufacture of chlorates appears, however, to be a combination of the above with the Weldon-Pechiney chlorine process. This is now being worked experimentally in France and England. Magnesia is suspended in water and saturated with chlorine, producing chloride and chlorate. Potassium chloride is added, forming potassium chlorate and magnesium chloride. After crystallising out the chlorate the solution is evaporated with the addition of magnesia, and the oxychloride thus formed heated in a current of air, forming chlorine and magnesia, as in the Weldon-Pechiney process. Thus both the magnesia and the chlorine are regained. Theoretically, this method will yield potassium chlorate *without consumption of chlorine*, by the combination of potassium chloride, through the agency of magnesia, with the oxygen of the air. The only apparent obstacle to the success of this remarkable process is the dense character of the magnesia resulting from the calcination of the oxychloride in a current of air at the high temperature necessary to liberate the chlorine. Such magnesia is but slowly acted upon by chlorine. Whether this obstacle can be overcome time alone will show.

Sodium chlorate has come into extensive use during the past few years as an oxidising agent in dyeing by means of aniline-black. For this purpose potassium chlorate is not sufficiently

<sup>1</sup> J. Soc. Chem. Ind., 1889, p. 524.

soluble. Owing to the difficulty of separating the very soluble sodium chlorate from solutions of sodium or calcium chlorides, this salt has until very lately been made at great expense from the potassium compound. Pechiney has, however, solved the problem of the industrial preparation of sodium chlorate; his process, now carried on extensively at his works at Salindres, France, is as follows:<sup>1</sup> Chlorine is passed into milk of lime, as usual, producing "chlorate liquor," containing five and one-half equivalents of chloride to one of chlorate. The liquor is then submitted to refrigeration, and at a temperature of 10° to 12° C. most of the calcium chloride crystallises out as the hydrated salt  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . By addition of lime to the liquor, and heating to 80° C., nearly all the remaining chloride is precipitated as oxychloride, and the resulting solution, after filtration, contains only three-tenths of one equivalent of chloride to one of chlorate. To this sodium sulphate is added, precipitating calcium sulphate and forming sodium chlorate; by evaporation this is obtained in well-formed cubical crystals, and is now sold at a price but little above that of the potassium salt.

Within the past two years potassium chlorate has been successfully manufactured by electrolysis. An account of the process will be found below.

*The Application of Electrolysis in Chemical Industry.*—Electro-metallurgy, or the separation of metals from their compounds by means of electricity, has long been practiced. In this way, early in the century, Davy first isolated potassium, sodium, lithium, calcium, and other metals. In modern times electric methods have been successfully applied in the separation and purification of the more common metals, especially zinc and copper, while electro-plating with various metals has become one of the commonest industries. With the development of modern dynamo-electric machines the cost of producing powerful currents of electricity has been enormously reduced, and new industrial applications of this force have quickly followed. Two metals, magnesium and aluminum, formerly reduced at high cost by means of sodium, are now cheaply obtained by electrolysis. Graetzel's electric process for the preparation of magnesium is now carried out on a large scale near Bremen, and the cheap metal so produced has supplanted that formerly obtained at Manchester and Boston by the old process of Caron and Deville. Within the past two years a company at Pittsburgh has succeeded in producing metallic aluminum at low cost by the electrolysis of fused cryolite, and is now manufacturing the metal on a considerable scale.

Many proposals have been made for decomposing common salt by an electric current, but the great power required and low price of the products obtained have heretofore made the industrial

<sup>1</sup> Weldon: J. Soc. Chem. Ind., 1882, p. 41.

application of the process quite hopeless. The subject of the electrolysis of chlorides has, however, received careful study of late, and it will perhaps be of interest to examine briefly the present aspect of this important question.

The first effect of the electrolysis of sodium chloride is, of course, the separation of sodium at the negative pole and the liberation of chlorine at the positive. If the action takes place in solution, however, the sodium set free will decompose the water present, forming sodium hydroxide and liberating hydrogen; if the electrodes are separated by a porous diaphragm, therefore, chlorine will be set free at the positive pole, while at the negative pole hydrogen will be given off and caustic soda will remain in solution. On the other hand, if the porous diaphragm is absent, the chlorine will react on the caustic soda, forming sodium chloride and sodium chlorate or hypochlorite, according to the temperature and strength of the solution.

The question of the power required for the decomposition of salt by electricity has lately been discussed in an interesting paper by Hempel.<sup>1</sup> His apparatus consisted of a cell divided by a porous partition of asbestos paper clamped between perforated electrodes, one of carbon and the other of sheet iron. The cell was filled with a solution of salt, which was kept saturated by automatic addition of dry salt. By the action of the current nearly pure chlorine was liberated at the carbon pole, while the opposite division of the cell became filled with a strong solution of caustic soda. A constant stream of carbon dioxide was passed into this solution, forming sodium carbonate, which was deposited in crystals and from time to time removed. The process was thus made continuous. Hempel found that one horse-power (calculated as equivalent to 680 volt-ampères) yielded 64.5 grams of chlorine and 259.8 grams of crystallised sodium carbonate ( $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ ) per hour. From this, assuming that equally good results could be obtained on a large scale, and calculating the alkali as soda-ash, we have:

1 h. p. = 1548 grams chlorine (= 3.41 lbs.), and 2308.8 grams soda-ash (= 5.09 lbs.) per day of 24 hours, or 586 h. p. = 1 ton chlorine and 1½ tons soda-ash per day. With coal at \$2.50 per ton, the cost of producing this power would be about 12 cents per h. p. per day, or, for 586 h. p., \$70.32 per day.

If one ton of chlorine is calculated as equivalent to three tons bleaching powder, the value of the products, at the present market rates in this country (soda-ash, \$30, and bleaching powder, \$35 per ton), would be about \$150, or more than twice the cost of the power. A liberal allowance must, however, be made for the expenses of the process and interest on the cost of plant, and it is not probable that the industry would prove remunerative unless a much cheaper source of power than steam can be made available.

<sup>1</sup> Ber. d. chem. Ges. 22, 2475.

It is not impossible that the use of very cheap fuel or water-power may make the electrolysis of salt practicable on a large scale.

In the case of potassium chloride, however, the conditions are much more favorable. Over 80,000 tons of this salt were produced at Stassfurt in 1889. A large part of this is converted by the Leblanc process into potassium carbonate, with the production of over 25,000 tons per year. The value of potash is at least five times that of soda ash, while the decomposition of potassium chloride by electrolysis is more easily accomplished than that of salt. Within the past year the electrolytic potash-process has been perfected, and is now in successful operation at Griessheim, near Frankfort. The power employed amounts to 1000 horse-power, and is generated by means of steam, using coal as fuel. There is reason to believe that this may be the process of the future for the production of potash from the chloride.

The subject of the electrolysis of chlorides without the use of a porous diaphragm, resulting in the formation of hypochlorite and chlorate as already explained, has received increased attention since the introduction of the *Hermite electric bleaching process*, patented in France, England and other countries in 1885. In this process a bleaching liquor is produced by the electrolysis of a solution of magnesium chloride. The apparatus consists of a trough containing the solution; the positive electrodes, consisting of a series of ebonite frames carrying sheets of platinum wire gauze, alternate with the negative electrodes formed of circular plates of zinc. The latter are kept in constant revolution, and any deposit which may become attached to them is removed by an ebonite knife bearing against each plate. The effect of the electrolysis is to produce a certain amount of magnesium hypochlorite. The solution is used directly for bleaching purposes, and re-electrolysed when its bleaching effect becomes feeble. The process has been introduced in a number of works in Europe, and also at two important manufactories near Boston; its chief use is the bleaching of wood-pulp in paper manufacture. The Hermite Company, in their Paris Exposition circular, offer to guarantee the production, every 24 hours, with nine horse-power and a current of 1000 ampères, of bleaching solution equal in efficiency to 100 kilos. of bleaching powder. Assuming 15 cents per horse-power as the cost of this power in a large plant, this claim is equivalent to that of the production of bleaching powder at \$13.50 per ton, or about one-third of its present price. The process has been severely criticised by Hurter, who carefully studied the whole subject of the electrolysis of magnesium chloride. He disputes the claims made by the advocates of the process, and shows that beyond a certain point very little hypochlorite is produced, the effect of the current after that being chiefly to produce chlorate and perchlorate. Hurter found that even in the production of a weak bleaching solution containing



two and a half grams of available chlorine per liter, only 20 per cent. of the current was effectively utilised.

Another important application of electrolysis, and one which offers good prospect of success, is the production of *potassium chlorate*. A process with this object has been perfected at Villers-sur-Hermès (Oise), France, by H. Gall and A. de Montlaur. As described in the patent, the process consists in submitting a solution of potassium chloride to electrolysis in a trough divided by a porous partition; the solution is caused to circulate between the two divisions of the cell in such a manner that the products of electrolysis react upon each other. The solution is kept at a temperature of  $50^{\circ}$ , in order to convert the hypochlorite formed into chlorate. Crystallised potassium chlorate produced by this process was exhibited at the Paris Exposition of 1889. It is stated that the inventors have secured a water-power equal to 1000 horse-power at Vallorbe, Switzerland, and are there erecting a large plant. The current employed is equal to 1000 ampères and 25 volts. One horse-power (requiring 25 kilos. of coal, if generated by steam) yields 1 kilo. of chlorate per day of 24 hours. If these statements are correct, and we assume 15 cents per horse-power per day as the cost of the power, this would correspond to 15 cents per kilo. of chlorate, or considerably below the present market price. With cheap water-power, therefore, there is every reason to believe that the process will be practically successful.

*Potassium Salts.*—Practically the whole of the world's supply of potassium salts is obtained from the following sources :

1. Leaching of wood-ashes.
2. The suint of sheep-wool.
3. The "vinasses" of the beet-sugar industry.
4. The Stassfurt salt-deposits.

From the first three sources, potash is obtained in the form of carbonate; from the Stassfurt deposits, in which it occurs as carnallite, or the double chloride of potassium and magnesium, the potash is obtained as chloride.

Owing to the rapid disappearance of the forests, the production of potash from wood-ashes, formerly extensively carried on in the United States, Canada, and several countries of Europe, has greatly decreased within the past few years, and is now insignificant in comparison with that from the last two sources mentioned. It is estimated that about 1750 tons of potash were produced from wood-ashes in the United States in 1887.

The production from the suint of sheep-wool is also comparatively unimportant, probably amounting to less than 1000 tons yearly, and is carried on chiefly in the wool-growing districts of France and Belgium. The potash is contained in the suint in the form of the salt of fatty acids, and constitutes nearly one-third the weight of the raw wool. The washings are evaporated and the



residue distilled in retorts, the ammonia and gases given off being utilised. Potash is obtained by leaching the carbonaceous residue left in the retorts.

The extraction of potash from the beet-root residues has been of great importance in the past, especially before the development of the Stassfurt deposits, and is still an industry of considerable magnitude. It is estimated that about 15,000 tons of potash are manufactured yearly from beet-root residues; chiefly in France and Germany. The industry is, however, not increasing, since the new processes for the extraction of crystalline sugar from the molasses (osmose and elution) yield the inorganic salts in a form better adapted to be returned to the soil as fertiliser. Before these processes were introduced the uncrystallisable beet-root molasses was universally submitted to fermentation for the manufacture of alcohol. After distilling off the alcohol so produced, the "vinasses" remaining, containing potash, ammonia salts, and various organic substances, were evaporated to dryness and calcined in open pans. By this method the volatile nitrogenous by-products were wholly lost. A great improvement in this process was introduced by Vincent, and is now employed on a large scale at Courrieres (Pas de Calais), France. This consists in distilling the residue from the evaporation of the vinasses in closed retorts. The volatile products, consisting of trimethylamine, ammonia, methyl alcohol, pyridine bases, etc., are condensed and purified. On repeated distillation, trimethylamine chloride breaks up into ammonia and methyl chloride. The latter is condensed into metal cylinders by pressure, and is now largely used in surgery to produce local anesthesia by the cold of its evaporation, and is also employed in the manufacture of coal-tar colors.

The crude potash remaining in the retorts after calcination contains about 32 per cent. of potassium carbonate, 13 per cent. of chloride, 18 per cent. of sulphate, and 12 per cent. of sodium carbonate.

The production of potassium salts from the Stassfurt deposits continues to increase, and this source now furnishes far more than all others. The total sales of crude potassium chloride at Stassfurt in 1889 amounted to 1,471,000 centners (1 centner = 110.2 lbs. av.) or 81,052 tons. Of this enormous quantity, it is estimated that 41.2 per cent. is consumed in the manufacture of nitrate by treatment with crude Chili saltpetre; 24.2 per cent. is converted into carbonate, chiefly by the Leblanc process; 20.4 per cent. is employed in agriculture, and 7.1 per cent. in the manufacture of bichromate and other salts of potassium.

The conversion of the potassium chloride of Stassfurt into carbonate is now almost universally accomplished by the Leblanc process. The industry was first established at Kalk, near Cologne, in 1863, and is now extensively carried on at that place, and also near Magdeburg and at Stassfurt, with a total

production of over 25,000 tons potassium carbonate per year. The decomposition of the chloride by sulphuric acid is accomplished in open roasters, similar to those formerly employed in the salt-cake process; the Mactear rotary furnaces are also successfully used. Revolving furnaces are employed for the conversion of the sulphate into carbonate, and the operations of leaching and calcination are similar to those followed in the soda industry. Potassium ferrocyanide is obtained from the mother-liquors as a by-product, and amounts to 1 per cent. of the potash produced.

Many attempts have been made to adapt the ammonia-soda process to the manufacture of potassium carbonate, but so far with slight success. Owing to the great solubility of potassium bicarbonate in a solution of ammonium chloride, potassium chloride cannot be treated in the same manner as salt. The use of trimethylamine in place of ammonia allows the precipitation of the potash as bicarbonate, but the *trimethylamine process*, which was tried on a commercial scale at Croix with good prospects of success, has lately been given up. It is said that the process has since been taken up experimentally by the Solvays at some of their works.

The Engel process, which also raised great expectations, consists in passing carbon dioxide into a solution of potassium chloride holding magnesia in suspension. A double carbonate of potassium and magnesium is precipitated, and magnesium chloride left in the solution. The double carbonate is decomposed by boiling with water, precipitating the magnesia as carbonate, while pure potassium carbonate, free from soda, is obtained by evaporating the solution. The magnesium chloride formed is discarded, and the magnesia required supplied in the form of calcined magnesite. The process was tried at Havre and at Stassfurt, but proved a failure from a commercial point of view. An improvement upon this method is said to be that of Borsche and Brünjes, in which ammonia and carbon dioxide are caused to react upon magnesia, and the resulting precipitate of ammonium-magnesium carbonate decomposed with potassium chloride. The Vereinigte Chemischen Fabriken at Stassfurt have recently begun the installation of this process on a large scale, but no information in regard to its practical working has yet been made public.

As stated under the head of "Electrolysis," the electric decomposition of potassium chloride is now being worked on a commercial scale near Frankfort, and there is good reason to expect that this method will play an important part in the potash industry.

Much valuable information in regard to the details of the various processes of manufacture of potassium salts is to be found in a work of Pfeiffer—*Die Kali-industrie*: Braunschweig, 1888.

SPENCER B. NEWBURY.

GRUNDLAGEN DER CHEMIE. Von D. MENDELEJEFF, Professor an der Universität in St. Petersburg. Aus dem Russischen übersetzt von L. JAWEIN, Docent am Technologischen Institut in St. Petersburg, und A. THILLOT, Assistent am chemischen Laboratorium des Technologischen Instituts in St. Petersburg. Carl Ricker, St. Petersburg, 1890.

Chemists are always glad to listen when Professor Mendelejeff speaks,—if he does not speak in his native language. The existence of a work on general chemistry, written by him in Russian, has been almost an aggravation to his admirers, and there has been, it may safely be asserted, a general desire to know what is in the work. Through this translation into German, and one into English already announced, we have it in our power to find out. The first number contains 144 pages, and the publishers announce that the book will be completed in eight numbers, to be issued in rapid succession at the price of three marks each. A table of contents of the entire work is given in lieu of a preface. This table is as follows :

Introduction.—Chapter I. Water and its Compounds.—Chapter II. Composition of Water. Hydrogen.—Chapter III. Oxygen and its Salt-forming Compounds.—Chapter IV. Ozone and Hydrogen peroxide. Dalton's Law.—Chapter V. Nitrogen and Air.—Chapter VI. Compounds of Nitrogen with Hydrogen and Oxygen.—Chapter VII. Molecules and Atoms.—Chapter VIII. Carbon and Hydrocarbons.—Chapter IX. Compounds of Carbon with Oxygen.—Chapter X. Sodium Chloride. Berthelot's Doctrine. Hydrochloric Acid.—Chapter XI. The Halogens: Chlorine, Bromine, Iodine, and Fluorine.—Chapter XII. Sodium.—Chapter XIII. Potassium, Rubidium, Cæsium, and Lithium. Spectroscopic Investigations.—Chapter XIV. Valency and Specific Heat of the Metals. Magnesium, Calcium, Strontium, Barium, and Beryllium.—Chapter XV. The Periodic Law of the Elements.—Chapter XVI. Zinc, Cadmium, and Mercury.—Chapter XVII. Boron, Aluminium and analogous Elements of the Third Group.—Chapter XVIII. Silicon and other Elements of the Fourth Group.—Chapter XIX. Phosphorus and other Elements of the Fifth Group.—Chapter XX. Sulphur, Selenium, and Tellurium.—Chapter XXI. Chromium, Molybdenum, Tungsten, Uranium, and Manganese.—Chapter XXII. Iron, Cobalt, and Nickel.—Chapter XXIII. Platinum Metals.—Chapter XXIV. Copper, Silver, and Gold.—Table of Atomic Weights.—Classification of the Elements into Groups.

The first number carries us through the Introduction, Chapter I, and a few pages of Chapter II. A careful reading of this number shows that the book is one of unusual interest and importance, as we had a full right to expect. There is thought in every line, and there is nothing chemistry is more in need of than clear thought. The author's mind is indeed so full of thoughts that he cannot find room for them in the text, and foot-notes abound to such an extent that considerably more than half the

matter is presented in this form, somewhat, it must be confessed, to the confusion of the reader. The book begins, for example, with these words: "Die Chemie beschäftigt sich mit der Erforschung homogener Stoffe, aus denen alle Körper der Welt zusammengesetzt sind." To these words are appended two long foot-notes in small type, covering nearly two full pages. One of these notes treats of the subject "Erforschung" and the other of "Stoffe" in a philosophical way. On the next page follow notes on "Körper," "Erscheinung," "Reaktion," "Chemische Erscheinung." This method of treatment is characteristic of the book. Under ordinary circumstances one would be disposed to complain, but, as the notes are, for the most part, of great interest and treat of important subjects in a clear, logical way, the inclination to complain gives way to a feeling of thankfulness that the notes have been written.

In these days when the physical side of chemical phenomena is receiving so much attention, the following words of Professor Mendelejeff will be read with special interest: "Die Natur der chemischen Kräfte ist für uns bis jetzt ebenso verborgen, wie die Natur der allgemeinen Schwere, aber auch ohne die Kenntniss derselben konnten, auf Grund mechanischer Begriffe die astronomischen Erscheinungen nicht nur unter ein einheitliches Prinzip gebracht, sondern auch in vielen Einzelheiten vorausgesagt werden; ebenso können auch in der Erforschung der chemischen Erscheinungen, ohne dass das Wesen der chemischen Verwandtschaft erkannt wird, dennoch, unter Anwendung der Gesetze der Mechanik, Dank der Fortschritten der mechanischen Wärmetheorie, bedeutende Erfolge erreicht werden. Bis jetzt ist dieser Theil der Chemie noch wenig ausgearbeitet und bildet, als nächste Aufgabe der Wissenschaft, ein besonderes Gebiet, das man theoretische oder physikalische Chemie, am richtigsten *Chemische Mechanik*, nennt. Das Studium dieses Theiles der Chemie setzt die Kenntniss der verschiedenen bis jetzt erhaltenen homogenen Körper, ihrer chemischen Umwandlungen und der sie begleitenden (thermischen und anderen) Erscheinungen voraus. Zweck des vorliegenden Werkes ist eben den Anfänger mit diesen chemischen Grundbegriffen vertraut zu machen." In a foot-note the author then states that in this book he will present only a few general conceptions of chemical mechanics. He says further: "Wie die Erfolge der Chemie zu Lavoisier's Zeiten einen fördernden Einfluss auf die gesammte Naturforschung ausgeübt haben, so muss, meiner Ansicht nach, eine selbständige chemische Mechanik neues Licht auf die gesammte molekulare Mechanik werfen, die als die Hauptaufgabe der modernen exakten Wissenschaft anzusehen ist."

In the chapter on water and its compounds there are extensive notes on *Dalton's law, the measurement of gas volumes, river water, potable waters, mineral waters, sea water, specific heat of water, dialysis, and solution*. The subject of solution is very fully



treated, nearly sixty pages of text and notes being given to this and the allied subjects, *water of crystallisation*, *cryohydrates*, and *hydrates*. As is well known, the author regards solutions as definite, liquid, chemical compounds in a state of dissociation, a conception which differs from that of Arrhenius as well as from that of Pickering. But he justifies his position by strong arguments based upon experiment, and it is certain that no one can deal with the subject of solution without taking into serious consideration the facts established by Mendelejeff.

Every teacher and every advanced student of chemistry should read and study this book with care. Even the most experienced teacher will find much in it that will prove of value to him.

I. R.

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CHEMICAL ARITHMETIC, Part I. A Collection of Tables, Mathematical, Chemical and Physical, for the Use of Chemists and others. By W. DITTMAR, LL. D., F. R. SS. Glasgow: William Hodge & Co., 1890. xvi + 175 pp. 8vo.

In the preface the author says: "The general idea by which I have been guided in its compilation is to try to offer to the scientific, as well as the technical, chemist a fairly complete collection of what he needs of mathematical auxiliaries and of chemical and physical constants in the ordinary routine of his laboratory work, and that *without going further*. This book, accordingly, does not pretend to compete with works of the order of Clarke's 'Constants of Nature,' or even of Landolt and Börnstein's 'Tabellen,' nor is it intended to supplant books which, like Lunge and Hurter's 'Pocket-Book,' address themselves to specialists in this or that branch of technical chemistry."

The book is evidently prepared with great care, and is arranged in a convenient form. There are four tables of logarithms, one of which, carried out to five places, is indexed to assist ready reference. Following these are tables giving the atomic weights of elements and the molecular weights of compounds, with the corresponding logarithms; analytical factors and their logarithms; factors used in the calculation of gas volumes; specific gravity tables; thermometer-correction formulae, etc. Almost every calculation which the average student of chemistry would be called on to make is here furnished. Nevertheless the special value of this work seems to lie rather in its accuracy than in its fulness. The paper and press-work are unusually good.

W. W. R.

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A TECHNOLOGICAL DICTIONARY OF INSURANCE CHEMISTRY. By WM. A. HARRIS. Liverpool: The Author, 1890. xi + 407 pp. 12mo.

This book takes up for discussion in alphabetical order all ordinary natural and artificial products, and especially the methods of

manufacture, of transportation and of storage employed, as well as the results of changes of temperature, etc., upon them, the object being to show in what respect these matters concern fire insurance companies. Such substances and mixtures of substances as are liable to what is ordinarily called "spontaneous combustion" are treated of with much detail. The transportation of fire by means of mill-dust, coal-dust, and the vapors of hydrocarbons, etc., is also discussed at length. The dangers attendant upon the transportation and storage of carelessly-packed cotton, hay, coal, petroleum, varnishes, etc., are described. Lists are given of what are commonly called explosives, and of such substances as under abnormal conditions become inflammable and explosive; in the case of "dangerous liquids" the flashing point, inflammation point and "relative degree of danger" are given. The risk introduced by the use of bull's-eyes in sky-lights and on board ships, and the consequent focusing of the sun's rays on inflammable material, is pointed out. These are, of course, but a few of the subjects treated.

The book is clear, well written, and, so far as examined, accurate. Where purely chemical matters are discussed, facts are stated simply, and the author wisely refrains from using chemical symbols, a stand which the majority of writers of popular works would do well to take. To the chemist this dictionary cannot fail to be of interest, and to those engaged in the business of insurance it would seem to be indispensable.

W. W. R.

OUTLINES OF GENERAL CHEMISTRY. By WILHELM OSTWALD. Translated, with the author's sanction, by JAMES WALKER, D. Sc., Ph. D. London: Macmillan & Co., 1890. xii+396 pp. 8vo. Price, 10/ net.

This is a translation of Prof. Ostwald's recently-published "*Grundriss der allgemeinen Chemie*." That the work of translation has been accomplished in a scholarly manner will appear evident to any one examining the book; while as regards its accuracy, it will suffice to say that the proof-sheets all passed through the author's hands and were approved by him.

W. W. R.

DIE EISENGALLUSTINTEN. Grundlagen zu ihrer Beurtheilung. Von O. SCHLUTTIG und G. S. NEUMANN. Dresden: v. Zahn & Jaensch, 1890. 97 pp. 8vo.

This book seems to be a very full treatise upon the subject of the iron-inks. The authors are chemists employed in the ink manufactory of Leonhardi, near Dresden, one of the largest establishments devoted to this industry in the world. They discuss the history of the manufacture of iron-inks; the legislation enacted by the Prussian Government looking to the employment of iron-rather than aniline- or chrome-inks; the advantages of the



former; the chemical process connected with their use; the various ingredients which go to make up the best inks, and the proportions in which these should be used; the classification of inks; the question of governmental inspection of inks, and the standards to be used in such inspection, etc. To a certain extent the book is controversial; nevertheless there is much contained in it which must prove of permanent value.

W. W. R.

A COMPEND OF CHEMISTRY, INORGANIC AND ORGANIC, INCLUDING URINARY ANALYSIS. By HENRY LEFFMANN, M. D. Third Edition, Revised. Philadelphia: P. Blakiston, Son & Co., 1890. 193 pp. 12mo.

In the preface the author says: "Books of this class do not always meet with favor at the hands of reviewers; but any one who has had experience in teaching at American medical colleges knows that as long as the present methods continue some such assistance is absolutely essential." With reference to the last clause one cannot help the remark "The more's the pity." Whatever else may be said of the book, it is certainly true that a medical student cannot learn chemistry by its aid. He may learn to make statements about such subjects as Valency and Radicles; but of what use is this to him or to anybody else? There is altogether too much in the book for the poor medical student. If all the purely theoretical matter had been omitted there would be less chance of harm being done. That this book, or something like it, is in demand is a most melancholy fact.

W. W. R.

PRINCIPLES OF GENERAL ORGANIC CHEMISTRY. By PROF. E. HJELT, Helsingfors. Translated from the Author's German edition of the original work, by J. Bishop Tingle, Ph. D., F. C. S., Assistant in the Laboratory of the Heriot-Watt College, Edinburgh. Longmans, Green & Co.: London and New York, 1890. 220 pp. 8vo.

Professor Hjelt's book "is intended for those students who have already some general elementary knowledge of organic chemistry, and who wish to extend and *systematise* that knowledge." Part I has to deal with the composition, constitution, and classification of organic compounds; Part II is devoted to illustrating the connection between the constitution of organic compounds and their chief physical properties; while Part III deals with the chemical behavior of organic compounds. In this Part the order of treatment is determined by the result of the reaction, and not the action of the reagent. The last is the most interesting division of the book. In it are discussed such subjects as the following: Oxidation, Reduction, Dehydration, Splitting off of Halogen Hydrides, Hydration processes, Union of Carbon with Carbon, Disruption of Carbon Bonds, etc. Each subject is treated simply and clearly, and the book cannot fail to prove interesting and profitable to students of chemistry.

I. R.

LESSONS IN ELEMENTARY CHEMISTRY, INORGANIC AND ORGANIC. By SIR HENRY E. ROSCOE, Emeritus Professor of Chemistry in Owens College, Manchester. New Edition, revised. London and New York: Macmillan & Co., 1890. 460 pp. 12mo.

This new edition of Roscoe's well-known book was prepared in 1885. In the preface, dated July, 1885, the author says: "In this edition, wholly reprinted, I have endeavored to place before the student all the important additions to the science which have been made since the last reprint. In the organic portion of the work, the necessary changes and additions are of greater extent than those in the less progressive inorganic department of the science." Any comment on the general character of this book would be superfluous, as it is familiar to all chemists. It is clear and succinct to a remarkable degree. While the succinctness is an advantage in so far as the book may be used for reference, it is, in the opinion of the writer of this notice, a decided disadvantage, in so far as the book is to be used for the purpose of studying chemistry. This is not so noticeable in the inorganic portion, but it is marked in the organic portion. So much is presented here that it is impossible to treat each subject satisfactorily. However, as an elementary presentation of the fundamental facts of chemistry the book is probably unsurpassed.

I. R.

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SUGAR ANALYSIS. For Refiners, Sugar-Houses, Experimental Stations, etc., and as a Handbook of Instruction in Schools of Chemical Technology. By F. G. WIECHMANN, Ph. D., Instructor in Chemical Physics and Chemical Philosophy, School of Mines, Columbia College; Consulting Chemist to the Havemeyers and Elder Sugar Refining Company, Brooklyn, N. Y. Wiley & Sons, New York, 1890. 187 pp.

To those in need of a concise, clear account of the methods of sugar analysis this book can be cordially recommended. According to the author, who has had much excellent practice in the line of work of which he treats, "the schemes selected and here offered, embrace those methods of analysis which, after careful investigation, and, in many cases, after prolonged trial in practice, have seemed to the writer best adapted to the requirements of a technical laboratory." References to original articles are given throughout the book, and at the end there is a list of books and of periodical literature bearing on Sugar Analysis. It would seem that the book contains everything that is likely to be needed by those for whom it is intended, and as the matter is presented in an orderly and clear way, the book must prove extremely useful.

I. R.

# AMERICAN CHEMICAL JOURNAL.

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## IS CHEMICAL ACTION AFFECTED BY MAGNETISM?

BY MORRIS LOEB.

The close relationship between electricity and chemical affinity on the one hand, and that between electricity and magnetism on the other, have naturally raised the question whether any relation can be traced between affinity and magnetism.

This question was the subject of numerous investigations during the entire first half of this century,<sup>1</sup> but appears to have dropped out of sight, until Prof. Remsen,<sup>2</sup> in 1882, again attracted attention to it by the interesting observation that, from a solution of the sulphate, copper is unequally deposited upon the armature of a horse-shoe magnet. Other experiments by Messrs. Nichols and Franklin,<sup>3</sup> and Messrs. Rowland and Bell,<sup>4</sup> have also borne relation to this question. I have nevertheless ventured to approach the subject from a new side, with the conviction that all of these investigations introduce phenomena which tend to obscure the point at issue, *i. e.* the effect of magnetism upon the chemical reaction itself. This will be made clear by an analysis of the principles upon which these investigations have been conducted: they can be divided into four categories.

The earliest experiments regarded the rusting of bar magnets; and the most trustworthy observers appear to invalidate the assertion of a few, that magnetised iron differs from the non-

<sup>1</sup> For full literature see E. Wartmann: *Phil. Mag.* **30**, 266.      <sup>2</sup> This *Journal* **3**, 137.

<sup>3</sup> *Am. J. Sci.* **34**, 419; **35**, 290.

<sup>4</sup> *Phil. Mag.* **26**, 105.

magnetised metal in this respect, or that the north and south poles show dissimilar behavior. The experiments were naturally crude, and a positive result, were it admitted, would obviously have been due to a polarised arrangement of the molecules, rather than to variations in chemical affinity.

Next came the crystallisation of salts or metals from a solution, within and without a magnet field. Quite a number of observers appear to have found that the *direction* of growth, either of the crystals themselves or of the clusters which they form, can be affected by the presence of a magnetic field, even though the substance be a diamagnetic. But what is there in this that involves a modification of chemical action? The quantity of deposit has not been observed to be altered by the magnet; the physical arrangement of the molecules during crystallisation is always governed by directive forces having no connection with affinity, and to the ordinary ones is now superimposed the polarising influence of the magnet.

A different principle is involved in Remsen's experiments, for they depend upon the removal of particles from a magnetised mass of iron, and the substitution therefor of faintly-magnetic copper. The explanation of Messrs. Rowland and Bell must appear highly plausible, that the resistance to such removal must protect the more highly magnetised points from reaction, so long as there are places where the iron can be more readily dissolved. We have here a purely mechanical reason for the localisation of the reaction, in a non-uniform field. That the *total* amount of reaction would not be affected we may infer from a recent experiment by Fossati,<sup>1</sup> in which he shows that the weight of iron precipitated from a solution by zinc is not affected by the presence of a strong magnetic field.

Apparently inconsistent with the protection-hypothesis are the observations of Messrs. Nichols and Franklin, which show that iron which has become passive through the action of strong nitric acid, suddenly regains its activity when introduced into a magnetic field. One might be tempted to ascribe this to the exposure of fresh surfaces, owing to the rearrangement of the molecules during magnetisation; but since the investigators have reason to seek the cause in the induction of local electric currents by the magnet,

<sup>1</sup> Bolletino dell' Elettrecista, 1890. I quote from Wiedemann's Beiblätter, 1890, p. 1010, which alone is at my disposal.

we may assign this phenomenon to the fourth category, that of galvanic action in the magnetic field. To my knowledge, Messrs. Nichols and Franklin were the first to experiment upon the effect of an unequal magnetic field upon an electrolyte: the movement of the paramagnetic salt to the interior portions of the field, and the inequality of electric potential consequent upon the variation of concentration, were proved, as might be expected. We have, then, this effect, as well as that of the Faradic induction, to account for any irregularities which the galvanoscope might indicate, when a solution undergoing electrolysis was also subjected to magnetic influence. Messrs. Nichols and Franklin do ascribe their observations to this cause, and see no reason to introduce a supposed change of the chemical conditions.

I fail to see any significance in the experiment of placing one of two gas-voltameters, or one of two cells containing an iron solution,<sup>1</sup> in a magnetic field, and looking for a difference in the amount of decomposition when a current is passed through the couple in series. Surely no such result could be expected in the face of the universally acknowledged Law of Faraday, unless, indeed, a magnetic field were imagined to alter the quantivalence of the elements.

To sum up: all experiments hitherto made have introduced non-chemical phenomena, due either to the inequalities of the magnetic field, or to the physical heterogeneity of the reacting system, or to both of these causes at once. It was my wish to study the effect of magnetism upon chemical reaction where the system remained homogeneous throughout, and where the field of stress was practically homogeneous. Such conditions can be realised by observing the speed of some reaction which does not involve solids, in the presence of a magnet, and, again, when there is no magnetic effect, provided the magnetic properties of the system could be altered by the reaction. In the same manner as an electric system is affected by its approach to or removal from a magnetic field, we might suppose that a reaction which made a system more or less amenable to magnetic action, might show evidence of acceleration or retardation by the magnetic force. If this effect were appreciable, the relation between magnetic force and affinity would be established, and data could be obtained for calculating the real value of magnetisation.

<sup>1</sup> Fossati.

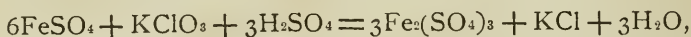


My results, however, have been negative, and I am led to believe that no such relation exists, unless it be so slight that my means of observation have been inadequate. Being confident, however, that my method has been of no lower order of delicacy than those hitherto employed in connection with the subject, I do not hesitate to assert that the interesting effects which have been noted are not due to a variation of affinity or of chemical reaction in its strictest sense. For this reason I herewith present my results.—

The choice of material for my investigation was rather limited: of all compounds, the salts of the iron group alone yield markedly paramagnetic solutions; furthermore, Wiedemann has shown that the ordinary form of reaction between salts does not affect the total magnetism of the system, so long as it involves merely an interchange of acids. But there is a marked change when the constitution of one of the ingredients is altered: the atomic magnetism of trivalent iron is 25 per cent. greater than that of the same element in the ferrous state. I resolved, therefore, to study the effect of magnetism upon the speed of oxidation and reduction of iron salts in solution by reagents which showed but a feeble magnetism by themselves.

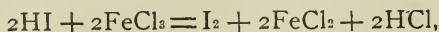
Two such reactions have already been studied under ordinary conditions, and, inasmuch as the methods employed seemed admirably suited to my purpose, I have followed them in this investigation.

Dr. J. J. Hood<sup>1</sup> determined the speed of the reaction



by estimating volumetrically with permanganate the amount of ferrous salt remaining unaffected at different stages of the process.

Meyerhoffer<sup>2</sup> gives one series of observations upon the reaction



in which case the iodine which had been set free could be determined with starch paste and sodic thiosulphate.

#### *Oxidation of a Ferrous Salt.*

I had at my disposal a large Ruhmkorff electro-magnet, with cylindrical iron cores ten inches long and three inches thick.

<sup>1</sup> Phil. Mag. [5] 6, 371; 8, 121; 13, 419.

<sup>2</sup> Ztschr. phys. Chem. 2, 597.



With the poles three inches apart, and with a current from ten storage cells, the intensity of the magnetic field was roughly determined at 10,000 c. g. s. per square-centimeter. For my supply of electricity I am indebted to the kindness of the director of the Physical Laboratory, Prof. A. A. Michelson. While ten cells were usually employed, I sometimes was enabled to use double that number, and in several instances obtained the current directly from the dynamo, employing as full a current as the apparatus would safely bear. Because the results were always virtually identical, no pains were taken to determine the exact strength of the magnetic field, but 18,000 c. g. s. is a low estimate of the maximum reached.

The axes of the cores being horizontal, a prismatic battery cell,  $2\frac{1}{2} \times 6 \times 6$  inches, was placed between the poles to serve as a bath of constant temperature. It was therefore protected from direct contact with the poles by thin layers of cotton batting, and was traversed by a rapid current of water from a reservoir whose contents were kept within  $0.1^\circ$  C. of the desired temperature.

The solutions were contained in a sort of pocket-flask of 100 cc. capacity, an inch thick, and having two flat sides of circular outline three inches in diameter. This flask was suspended in the bath in such a manner as to be just between the poles of the magnet. The solutions which were not to be subjected to the influence of the magnet were contained in a precisely similar flask, and the water-bath in which this was placed was fed by the overflow from the first mentioned one. Where it was not feasible to observe the two reactions at the same time, especial care was taken to keep the temperature constant.

The following solutions were employed: a  $\frac{1}{3}$ -molecular solution of potassium chlorate, a  $\frac{1}{2}$ -molecular solution of sulphuric acid, a  $\frac{1}{2}$ -molecular solution of ferrous sulphate, a solution of potassium permanganate of which 12.5 cc. corresponded to 1 cc. of the iron solution. The latter was made from crystallised ferrous sulphate, with a little sulphuric acid and an excess of metallic iron, so that it was very nearly neutral.

Proper volumes of the chlorate and the acid solutions having been run into the flask and sufficient water to make the volume 80 cc., the solution was allowed to acquire the temperature of the water-bath. Thereupon 20 cc. of the ferrous sulphate solution, which had been brought to the same temperature, were added

rapidly, the flask was vigorously shaken, and at once replaced in the water-bath. If the magnet was to be employed, its electric circuit was closed at this time. After the expiration of a few minutes, 10 cc. were withdrawn from the flask by means of a pipette, and were quickly run into a large quantity of cold water contained in a porcelain dish, the time being noted when the pipette was emptied. The titration was then executed as rapidly as possible. This operation was repeated at suitable intervals, until the solution was exhausted or external conditions prevented a continuation of the observation. Where two reactions were to be observed together, the second solution was mixed ten minutes after the first, the same interval being preserved, as nearly as might be, throughout. Owing to the weakness of the permanganate solution and to varying conditions of illumination, my titrations have a probable error of fully  $\frac{1}{20}-\frac{1}{15}$  cc., but this is in no unfavorable proportion to the observed values; in cases of overcoloration I rejected the result, rather than titrate back with another solution.

The reaction has been proved by Hood to be subject to the law

$$\frac{dx}{dt} = C(A-x)(B-x),$$

where  $x$  = the amount of substance changed,  $t$  = time elapsed,  $A$  and  $B$  represent the original quantities of ferrous sulphate and chlorate respectively, and  $C$  is a coefficient depending on external circumstances.

As equivalent quantities of  $A$  and  $B$  were used,

$$\frac{dx}{dt} = C(A-x)^2.$$

Integrating,  $\frac{1}{A-x} = Ct + \text{constant}.$

Calculating this constant from the initial conditions  $d=0$ ,  $x=0$ ,  $\text{constant} = \frac{1}{A}$ , and consequently

$$C = \frac{1}{At} \cdot \frac{x}{A-x}.$$

$A$  is the amount of permanganate required at the first titration, and  $A-x$  represents the amount of each subsequent one, after the lapse of  $t$  minutes. We possess all the data for calculating  $C$ . This coefficient has been shown by Hood to depend upon the temperature, to be augmented by the presence of free

acid, and diminished by the presence of neutral salts not participating in the reaction. It is consequently decreasing continually during the reaction, most noticeably, however, toward the end. Furthermore, if magnetism is of influence, the values of  $C$  must show it. In order to eliminate the other influences, I have sought to take the samples from corresponding solutions at the same intervals of time, and have varied the conditions somewhat by changing the temperatures as well as the amounts of sulphuric acid present in different series.<sup>1</sup> It will be seen that, while there is considerable variation between individual determinations, these variations are no greater between analogous samples of two corresponding series than between two succeeding samples of the same series. Further, the means of the whole series agree well with each other. The tables which I subjoin are selected, solely with reference to their general reliability, from a larger mass of material, all of which gave analogous results. While the effect of magnetism should produce acceleration, the variations of  $C$  from that of the non-magnetic reaction are negative quite as frequently as positive.

Series I.— $\text{KClO}_3 + 6\text{FeSO}_4 + 3\text{H}_2\text{SO}_4$ . Temperature,  $10.2^\circ$ .

Series II.—Same conditions, in magnetic field (10 cells).

$t$ .		$A - x$ .		$C$ .	
I.	II.	I.	II.	I.	II.
0	0	24.38	24.26	...	...
30.25	29.75	22.78	22.88	.049524	.048357
105	104.25	20.22	20.28	8050	7940
155.17	154.86	18.71	18.68	8011	7951
210	210	17.49	17.27	7695	7942
241	241.33	16.82	16.79	7546	7599
305.25	305.5	15.64	15.53	7491	7584
		Mean, . . . . .		.048051	.047895
		Mean of last five, .		.047758	.047803

Series III.—Same relation,  $\text{KClO}_3$ ;  $\text{FeSO}_4$ ; great excess  $\text{H}_2\text{SO}_4$ . Temperature,  $18.7^\circ$ .

Series IV.—Same as III, but with magnet (20 cells).

Series V.—Same as III, but with magnet (dynamo).

<sup>1</sup> In this connection it may be interesting to note that this reaction is, according to my experiments, barely perceptible at  $0^\circ \text{C}$ .—a result which agrees closely with the limit set by Dr. Hood by extrapolation with his temperature-coefficient.

<i>t.</i>			<i>A - x.</i>			<i>C.</i>		
III.	IV.	V.	III.	IV.	V.	III.	IV.	V.
0	0	0	23.16	23.10	23.10	...	...	...
20	20	20.5	18.57	18.39	18.32	.035335	.035543	.035509
40	40	40	15.33	15.45	15.41	5513	5358	5400
60	60	60	13.28	13.38	13.21	5353	5241	5401
80	80.5	80	11.71	11.58	11.42	5276	5348	5534
100	100.25	100	10.41	10.45	10.40	5288	5227	5286
120	120	120	9.38	lost.	9.45	5282	...	5211
139.75	130.75	140	8.72	8.99	8.54	5116	5197	5272
160.25	155	161	7.94	8.17	7.84	5164	5104	5233
						Mean, .035292	.035288	.035355

### *Reduction of Ferric Chloride.*

The reaction  $2\text{HI} + 2\text{FeCl}_3 = \text{I}_2 + 2\text{FeCl}_2 + 2\text{HCl}$ , is not a simple one, being reversible, and furthermore accompanied by complicating bye-reactions. It seemed better to avoid all attempts to obtain the reaction-coefficients, and to make parallel experiments, with exactly the same time-intervals. If the magnetic force had any effect, this must be visible from the burette-readings.

The method used was exactly as before, but diluted solutions were employed to prevent the loss of free iodine. Equivalent quantities of hydriodic acid and ferric chloride were allowed to react in  $\frac{1}{100}$ -molecular solutions, and 10 cc. were taken out at a time and titrated with  $\frac{1}{115}$ -normal sodium thiosulphate solution. The determinations were very exact, and the corresponding burette-readings will be found to correspond so closely as to leave no doubt of the exact equality of speed within and without the magnetic field. I give all the series which were observed; in the second set, the reaction was carried as far as it would go—at least there was no more iodine liberated after  $15\frac{3}{4}$  hours' standing.

Temperature,  $17.8^\circ$ .

Without Magnet.		With Magnet (dynamo).	
Time.	$\text{Na}_2\text{S}_2\text{O}_3$ required.	Time.	$\text{Na}_2\text{S}_2\text{O}_3$ required.
30.5	3.89	30.5	3.95
60	4.80	60	4.52
120	5.10	120	5.10
180	5.55	180	5.40
231	5.60	231	5.58

Same conditions.

Time.	Without Magnet. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> required.	Time.	With Magnet (dynamo). Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> required.
40	5.99	40	5.92
86	6.92	85	6.93
130	7.38	130	7.38
205	7.85	205	7.90
266	8.07	266	8.04
325	8.28	325	...
375	8.32	375	8.30
...	...	1330 <sup>1</sup>	8.28

Same proportions ; temperature, 0°.

Time.	Without Magnet. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> required.	Time.	With Magnet (10 cells). Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> required.
60	2.70	60.5	2.80
120	3.72	120	3.70
195	4.54	195	4.42
275	4.86	275	4.90
360	5.20	...	...
380	5.70	380	5.80
480	6.06	480	6.10
600	6.43	600	6.60
705	6.71	705	6.75

CHEMICAL LABORATORY, CLARK UNIVERSITY.

Contributions from the Laboratory of Cornell University.

## DECOMPOSITION OF SOME DIAZO COMPOUNDS OF NAPHTHALENE WITH ALCOHOL.<sup>2</sup>

BY W. R. ORNDORFF AND F. L. KORTRIGHT.

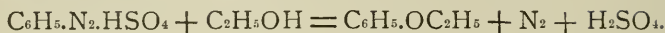
It has been known for some time that when the salts of diazo compounds of benzene are decomposed with alcohol, two reactions may take place. The diazo group may be replaced by hydrogen, according to the equation



<sup>1</sup> Without magnet.

<sup>2</sup> Prof. Remsen kindly informed the authors of this paper that the work on the decomposition of the diazo compounds of naphthalene would not be taken up in the Johns Hopkins Laboratory.

or the ethoxy group may enter the compound, thus :



Sometimes both of these reactions take place simultaneously, but generally one or the other prevails.

It is a matter of considerable interest and importance to determine exactly the conditions which give rise to each of these reactions, and though considerable work has been done on this subject, chiefly by Remsen and his pupils, it cannot be said that the problem is as yet by any means solved.

Thinking that the study of the decomposition of the diazo compounds of naphthalene with alcohol might throw some light on this question, the following investigation was undertaken. There are, to be sure, a large number of decompositions of the diazo compounds of naphthalene recorded in the literature, but in few cases is any attention paid to anything save the first reaction, or rather to the products resulting in accordance with the first reaction, and but rarely is any statement made as to the yield obtained. In most cases the reaction has merely served as a means of introducing a hydrogen atom in place of the diazo group, and groups (like the amido and nitro groups), which can readily be converted into the diazo group. Hence the other products formed at the same time were of but little interest, and they have not been isolated or studied. So long as the reaction with alcohol furnished enough material to work with, no attention was paid to the yield.

In the following work the decomposition of some of the simpler diazo-naphthalene compounds with alcohol has been studied, but every product of the reaction has been carefully isolated and examined, and the attempt has been made to obtain, as far as possible, quantitative results. While it is not assumed that these results are more than approximately correct, it is thought that they may be used to give some idea of the course of the reaction.

#### *Preparation of $\alpha$ -Diazo-naphthalene Sulphate.*

10 grams of the commercial  $\alpha$ -naphthyl amine (melting-point,  $45^\circ$ - $47^\circ$ ) were rubbed up with water to a thin paste, 40 grams of concentrated sulphuric acid added, and the whole well ground together in a mortar. Nitrous fumes, obtained in the usual manner from arsenic trioxide and nitric acid, were then passed



into the mixture until they ceased to be absorbed. Care was taken to keep the mixture cool by surrounding it with ice-water and constantly agitating while the nitrogen trioxide was being absorbed. The liquid was then quickly filtered by suction to remove any decomposition products, and the filtrate treated with alcohol and ether, and cooled in a freezing mixture of ice and salt until all the diazo-naphthalene sulphate had crystallised out. The crystals were washed with alcohol and ether and dried on porous paper in the air. From 10 grams of  $\alpha$ -naphthyl amine 14 grams of the dry diazo-naphthalene sulphate were obtained, *i. e.* about 79 per cent. of the theoretical yield.

$\alpha$ -diazo-naphthalene sulphate, thus prepared, crystallises in light-yellow, flat needles which retain their yellow color even after being recrystallised from water several times. It is very soluble in water, only slightly so in alcohol, and insoluble in ether. If exposed to the light it rapidly turns green, although it may be preserved for some time if kept in the dark. When heated to  $115^\circ$  it puffs feebly, leaving a black, charred mass, but it does not explode by percussion. An attempt was made to analyse the  $\alpha$ -diazo-naphthalene sulphate by the usual method of decomposing the salt with water and collecting and measuring the nitrogen given off. But the results were always too low, probably owing to the formation of an azo dye by the combination of some of the undecomposed diazo salt with the  $\alpha$ -naphthol which is formed by the decomposition of  $\alpha$ -diazo-naphthalene sulphate with water. It was hence impossible to estimate anything but the acid, and this was done by precipitating with barium chloride and weighing the barium sulphate formed.

I. 0.2505 gram substance gave 23.3 cc. nitrogen at  $21^\circ$  and 732 mm. bar.

II. 0.2325 gram substance gave 21 cc. nitrogen at  $19^\circ$  and 733 mm. bar.

III. 0.2185 gram substance gave 19 cc. nitrogen at  $22^\circ$  and 735 mm. bar.

IV. 0.1455 gram substance gave 13.6 cc. nitrogen at  $19^\circ$  and 738 mm. bar.

V. 0.188 gram substance gave 0.174 gram barium sulphate.

	Calculated for $C_{10}H_7.N_2.HSO_4$ .	I.	II.	Found. III.	IV.	V.
N	11.11	9.78	9.70	9.20	10.17	...
SO <sub>3</sub>	31.74	...	...	...	...	31.78

*Decomposition of  $\alpha$ -diazo-naphthalene sulphate in alcohol.*—10 grams of the dry  $\alpha$ -diazo-naphthalene sulphate and 250 cc. of absolute alcohol were placed in a 500-cc. round-bottomed flask which was connected with a reflux condenser and heated at from  $70^{\circ}$  to  $75^{\circ}$  on the water-bath. At about  $70^{\circ}$  a strong evolution of nitrogen began, and continued without further heating until the diazo salt was completely in solution. The alcohol was colored red, the color becoming deeper and deeper as the reaction proceeded, and the odor of aldehyde was distinctly perceptible throughout the whole experiment. When the evolution of nitrogen had ceased, the contents of the flask were boiled to insure complete decomposition. The excess of alcohol was then distilled off and kept for use in the next decomposition. Here again the odor of aldehyde was distinctly perceptible in the alcoholic distillate.

In this manner 50 grams of the  $\alpha$ -diazo-naphthalene sulphate were decomposed. The last alcoholic distillate was diluted with water and a small quantity of naphthalene thus obtained. The total residue from the decomposition of the  $\alpha$ -diazo-naphthalene sulphate was then placed in a liter round-bottomed flask and distilled in steam from an acid solution. The residue left in the flask consisted of tarry material and any amido compounds that might be present. The distillate was made alkaline with sodium hydroxide and again distilled in steam. The non-volatile residue left after this distillation was evaporated down to small bulk and acidified with hydrochloric acid; the odor of  $\alpha$ -naphthol was noticed, and after a time a few crystals of this substance were deposited, but sufficient to weigh could not be obtained.

By this method of procedure the final distillate was freed from amido and phenol-like bodies. The distillate was now separated by fractioning in steam. A solid passed over first and solidified before leaving the condenser, while the other product followed more slowly as an oil; so that the first receiver contained nothing but the solid, the last an oil, and the intermediate receivers a mixture of the two. By repeating the process with the contents of the intermediate receivers a further separation was made, and after five distillations a complete separation was obtained. The solid was recrystallised from alcohol, and found to form colorless, shining plates, melting at  $81^{\circ}$ . An analysis gave the following results:

0.228 gram substance gave 0.7860 gram  $\text{CO}_2$  and 0.1265 gram  $\text{H}_2\text{O}$ .

	Calculated for $C_{10}H_8$ .	Found.
C	93.75 per cent.	93.99 per cent.
H	6.25	6.16

From the physical properties, including the melting-point, and the results of the analysis, there can be no doubt that the substance is naphthalene.

The substance supposed to be ethoxy-naphthalene was dehydrated by dissolving in ether and heating the ethereal solution with calcium chloride. The ether was then distilled off and the oil rectified. Thus prepared, the substance is a light-yellow liquid of a peculiar odor and having a specific gravity of 1.074 at  $0^\circ$  compared with water at  $4^\circ$ . It has the boiling-point  $276^\circ$ , the mercury column being completely in the vapor and the barometric pressure being 745 mm. On exposure to light the oil rapidly turns green. An analysis gave the following results:

0.223 gram substance gave 0.688 gram  $CO_2$  and 0.139 gram  $H_2O$ .

	Calculated for $C_{10}H_7 \cdot O \cdot C_2H_5$ .	Found.
C	83.72 per cent.	84.13 per cent.
H	6.98	6.92

From the results of this analysis and the physical properties, there can be no doubt that the substance is the  $\alpha$ -ethoxy-naphthalene first prepared by Schaeffer.<sup>1</sup> As the description given in the literature of the properties of this ether is very meagre, it was thought advisable to prepare it for the purpose of comparison with the product obtained from the decomposition of the  $\alpha$ -diazo-naphthalene sulphate with alcohol. The method recommended by Dr. Henriques<sup>2</sup> for the methyl ether of  $\alpha$ -naphthol was employed. 30 grams of  $\alpha$ -naphthol, 30 grams of absolute alcohol, and 13 grams of concentrated sulphuric acid were mixed in a 500-cc. round-bottomed flask and heated at  $140^\circ$  for 4 hours on a paraffin-bath. The contents of the flask were then poured into water, the lower layer separated, washed with solution of sodium hydroxide, then with water, and finally distilled in steam. The  $\alpha$ -ethoxy-naphthalene was then separated from the water by dissolving in ether. The ethereal solution was freed from water by means of calcium chloride. After distilling off the ether, 18 grams of the ethoxy-naphthalene remained. This boiled at  $277^\circ$ , the mercury column being entirely surrounded by vapor

<sup>1</sup> Ann. Chem. (Liebig) 152, 286.

<sup>2</sup> Ibid. 244, 72.

and the barometric pressure being 748 mm. The liquid had a specific gravity of 1.0746 at 0° compared with water at 4°; turned green by standing in the light; and generally agreed in physical properties with the  $\alpha$ -ethoxy-naphthalene obtained from the decomposition of  $\alpha$ -diazo-naphthalene sulphate in alcohol. 50 grams of the  $\alpha$ -diazo-naphthalene sulphate yielded 10 grams of naphthalene and 8 grams ethoxy-naphthalene. This is equivalent to a conversion of 40 per cent. of the  $\alpha$ -diazo-naphthalene sulphate into naphthalene and 23 per cent. into the ethoxy-naphthalene.

*Decomposition of  $\alpha$ -diazo-naphthalene sulphate in water.*—A portion of the  $\alpha$ -diazo-naphthalene sulphate was heated with water. At about 80°–90° nitrogen was given off and a quantity of red coloring matter and tar formed. The liquid was filtered while hot, and from the filtrate, on cooling, a quantity of shining plates separated out. These had the melting-point of 96°, and had the odor and general properties of  $\alpha$ -naphthol.

*Preparation of  $\beta$ -Diazo-naphthalene Sulphate.*

The  $\beta$ -naphthyl amine used was the commercial product and melted at 108°–110°. Several methods of preparation of the diazo-naphthalene sulphate were tried before a satisfactory one was found. Unless a considerable excess of sulphuric acid was used, much red material was formed, and the diazo-naphthalene nitrate was apt to crystallise out. The nitric acid either was carried over mechanically from the flask in which the nitrogen trioxide was generated, or was formed by the decomposition of the nitrogen trioxide and tetroxide by water.<sup>1</sup> The diazo nitrate, being much less soluble than the sulphate, crystallised out on standing. Both these difficulties were overcome, however, by adding a large excess of sulphuric acid. The best results were obtained by using four times as much concentrated sulphuric acid by weight as naphthyl amine. From 10 grams of  $\beta$ -naphthyl amine 13 grams of  $\beta$ -diazo-naphthalene sulphate were obtained, which is about 74 per cent. of the theoretical yield. The general details of the method are the same as in the case of the  $\alpha$ -diazo-naphthalene sulphate. The diazo salt was washed with alcohol, then with ether, and finally dried before being used. An analysis gave the following results:

I. 0.148 gram gave 14.6 cc. nitrogen at 17° and 754 mm. bar.

<sup>1</sup> Remsen's Advanced Inorganic Chemistry, p. 287.

- I. 0.148 gram gave 0.0573 gram  $\text{H}_2\text{SO}_4$ .  
 II. 0.167 gram gave 16.1 cc. nitrogen at  $17^\circ$  and 754 mm. bar.  
 II. 0.167 gram gave 0.0652 gram  $\text{H}_2\text{SO}_4$ .

	Calculated for $\text{C}_{10}\text{H}_7\text{N}_2\cdot\text{HSO}_4$ .	I.	Found.	II.
N	11.11 per cent.	11.21 per cent.	10.98 per cent.	
$\text{SO}_3$	31.74	31.63	31.88	

*Properties of  $\beta$ -diazo-naphthalene sulphate.*—The  $\beta$ -diazo-naphthalene sulphate is soluble in water, very slightly soluble in alcohol, and insoluble in ether. It crystallises out from its aqueous solution on the addition of alcohol and ether, and cooling, in flat, needle-shaped yellow crystals. By careful recrystallisation from water these may be obtained nearly colorless, but immediately turn yellow on exposure to the light. The crystals are biaxial, with inclined extinction, and probably belong either to the monoclinic or to the triclinic system. Left exposed to light and air, they rapidly change from yellow to green, and finally to a dark-brown color. This decomposition was shown to be due to the effect of light, and at ordinary temperatures air and moisture have no effect on the salt. On being heated the salt explodes feebly when the temperature reaches  $115^\circ$ . It does not explode by percussion, however.

*Decomposition of  $\beta$ -diazo-naphthalene sulphate in alcohol.*—30 grams of the  $\beta$ -diazo-naphthalene sulphate were decomposed in 10-gram portions in precisely the same manner as the  $\alpha$ -diazo-naphthalene sulphate. The alcohol, after the decomposition, was of a deep-red color, and the odor of aldehyde was faintly perceptible. The residues were united and, after dilution with water, were distilled with steam from a solution made alkaline with sodium hydroxide. The non-volatile residue left in the flask was concentrated by evaporation, filtered to free it from tarry matter, and the filtrate acidified with hydrochloric acid. A precipitate was thus obtained which was filtered off and recrystallised from hot water. The substance then crystallised in colorless shining plates, which melted at  $121^\circ$ , and had the odor and general physical and chemical properties of  $\beta$ -naphthol. The distillate contained now two substances, one of which seemed to be naphthalene, and the other the  $\beta$ -ethoxy-naphthalene. These were separated by fractioning in steam, the method used being essentially the same that was employed in the separation of the naphthalene



from the  $\alpha$ -ethoxy-naphthalene, except that here we have to deal with two solids with different melting-points instead of a solid and a liquid. By properly adjusting the temperature of the condenser, however, it was possible to cause one substance (the naphthalene) to solidify before leaving the condenser, and the other ( $\beta$ -ethoxy-naphthalene) to remain liquid until it reached the receiver, and by this means the point of separation could be determined. The substance supposed to be naphthalene crystallised from alcohol in colorless shining plates, melting at  $81^\circ$ . An analysis gave the following results:

0.22 gram gave 0.7545 gram  $\text{CO}_2$  and 0.125 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{10}\text{H}_8$ .	Found.
C	93.75 per cent.	93.53 per cent.
H	6.25	6.30

The substance is evidently naphthalene.

The other substance, supposed to be the  $\beta$ -ethoxy-naphthalene, crystallised from alcohol in colorless shining plates which gradually turn brown on exposure to the light. When perfectly dry these crystals melted at  $37^\circ$ . They are soluble in alcohol, ether, carbon bisulphide, toluene, petroleum-ether, etc., but insoluble in water. An analysis gave the following results:

0.257 gram gave 0.784 gram  $\text{CO}_2$  and 0.159 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{10}\text{H}_7\text{O.C}_2\text{H}_5$ .	Found.
C	83.72 per cent.	83.19 per cent.
H	6.98	6.87

There can be no doubt from these results that the substance is the  $\beta$ -ethoxy-naphthalene. *plus in solution*

*Decomposition of  $\beta$ -diazonaphthalene sulphate by water.*—A portion of the  $\beta$ -diazonaphthalene sulphate was heated with water. Between  $80^\circ$  and  $90^\circ$  nitrogen was given off in large quantity and at the same time red material and tar were formed. On filtering the hot solution and allowing the filtrate to cool, shining plates crystallised out. These had the melting point ( $121^\circ$ ), odor and general properties of  $\beta$ -naphthol. *p. 366*

*Decomposition of the  $\beta$ -diazonaphthalene sulphate with hydrochloric acid.*—13 grams of the  $\beta$ -diazonaphthalene sulphate were treated with 200 cc. of 40-per cent. hydrochloric acid, and allowed to stand for several weeks. The flask was then found to be filled with fine crystals. The solution was then treated with an excess



of sodium hydroxide and distilled in steam. A solid distilled with the steam, and this had a pink color which was, however, removed by a second distillation in steam. On recrystallising from alcohol, plate-like crystals with a pearly lustre were obtained, which melted at  $59^{\circ}$ , and showed all the other properties characteristic of  $\beta$ -chlor-naphthalene. From 13 grams of the diazo salt 4 grams of the  $\beta$ -chlor-naphthalene were obtained, corresponding to a yield of about 50 per cent. of the theoretical quantity. Liebermann<sup>1</sup> prepared  $\beta$ -chlor-naphthalene by boiling the  $\beta$ -diazo-naphthalene sulphate with concentrated hydrochloric acid, but obtained only a small yield of the  $\beta$ -chlor-naphthalene. It would seem, therefore, preferable to allow the decomposition to proceed at ordinary temperatures in this case. A considerable quantity of  $\beta$ -naphthol was formed in this decomposition also.

*Preparation of  $\beta$ -Diazo-naphthalene Nitrate.*

10 grams of  $\beta$ -naphthyl amine were well rubbed up with water in a mortar, and an equal weight of nitric acid (sp. gr., 1.426) added, care being taken to keep the mixture cool to prevent the formation of nitro compounds. This mixture was then diazotised, and the precipitate of the diazo salt filtered off and recrystallised from water at  $40^{\circ}$ , by adding alcohol and ether to the aqueous solution and cooling. 10 grams  $\beta$ -naphthyl amine gave 8 grams  $\beta$ -diazo-naphthalene nitrate—about 53 per cent. of the theoretical yield. An analysis of the salt gave the following results :

0.15 gram salt gave 17.8 cc. nitrogen at  $20.5^{\circ}$  and 747 mm. bar.  
0.192 gram salt gave 0.0549 gram  $\text{HNO}_3$ .

	Calculated for $\text{C}_{10}\text{H}_7\text{N}_2\text{NO}_3$ .	Found.
N	12.90 per cent.	12.99 per cent.
$\text{NO}_3$	28.57	28.21

*Properties of  $\beta$ -diazo-naphthalene nitrate.*— $\beta$ -diazo-naphthalene nitrate is soluble in water at ordinary temperatures, but crystallises out when the solution is cooled. It is only slightly soluble in water containing a mineral acid, and is insoluble in absolute alcohol and ether. From water it crystallises in hard, warty crystals. From water to which alcohol and ether have been added, it crystallises in flat yellow needles. It decomposes in the light, turning red; but air and moisture produce little or no effect,

<sup>1</sup> Ann. Chem. (Liebig) 183, 270.

provided light be excluded. It explodes violently when heated to  $100^{\circ}$ , and also by percussion.

*Decomposition of the  $\beta$ -diazo-naphthalene nitrate in alcohol.*—50 grams of the  $\beta$ -diazo-naphthalene nitrate were decomposed, in 10-gram portions, in the same manner as described for the  $\alpha$ -diazo-naphthalene sulphate. The odor of aldehyde was quite perceptible during the decomposition. The alcohol was then distilled off, and the residue diluted with water and distilled in steam from an acid solution. From the non-volatile residue in the flask  $\alpha$ -nitro- $\beta$ -naphthol and  $\alpha^1\alpha^1$ -dinitro- $\beta$ -naphthol were obtained in small quantity.

The solids, filtered off from the distillate, were separated by fractioning in steam, as before, into naphthalene and  $\beta$ -ethoxy-naphthalene. 50 grams of  $\beta$ -diazo-naphthalene nitrate gave 10 grams of ethoxy-naphthalene and only 2 grams naphthalene. This is equivalent to a conversion of about 26 per cent. of the  $\beta$ -diazo-naphthalene nitrate into  $\beta$ -ethoxy-naphthalene and 7 per cent. into naphthalene. The decomposition of the  $\beta$ -diazo-naphthalene nitrate with water was then shown to be analogous in every respect to the decomposition of the  $\beta$ -diazo-sulphate with water,  $\beta$ -naphthol being formed.

#### *Preparation of $\beta$ -Ethoxy-naphthalene.*

Since the  $\beta$ -ethoxy-naphthalene obtained by the decomposition of the diazo compounds with alcohol, had a melting-point of  $37^{\circ}$  instead of  $33^{\circ}$ , as given by Schaeffer and others, it was thought advisable to prepare some of the  $\beta$ -ethoxy-naphthalene by another method and compare it with that obtained from the decomposition of the diazo compounds. The method used was that recommended by Schaeffer:<sup>1</sup> 28 grams of the  $\beta$ -naphthol were dissolved in alcohol with 11 grams of potassium hydroxide, and 24 grams of ethyl bromide were added. After boiling this mixture in a flask provided with a reflux condenser, for 3 hours, the potassium bromide was filtered off and the ethoxy-naphthalene distilled in steam. It was then recrystallised from alcohol. It crystallised in shining plates which melted sharply at  $37^{\circ}$ , even after it had been recrystallised several times from alcohol, and dried in a desiccator over sulphuric acid. Like the ethoxy-naphthalene obtained from the diazo compounds, it gradually turned brown

<sup>1</sup> Ann. Chem. (Liebig) 152, 287.

in the light; was soluble in alcohol, ether, carbon bisulphide, toluene, petroleum-ether, etc., but insoluble in water. Moreover it resembled the  $\beta$ -ethoxy-naphthalene in general appearance, and had the same odor.

*Summary.*

The results of this work may be summed up as follows :

The  $\alpha$ -diazo-naphthalene sulphate is easily prepared, and when decomposed by alcohol, about 40 *per cent.* is converted into naphthalene and 23 *per cent.* into the ethyl ether of  $\alpha$ -naphthol. The  $\beta$ -diazo-naphthalene sulphate and nitrate are rather more difficult to prepare. The sulphate when decomposed with alcohol yields about 30 *per cent.* in the form of the ethyl ether of  $\beta$ -naphthol and 7 *per cent.* in the form of naphthalene, a small quantity of  $\beta$ -naphthol being formed at the same time. The  $\beta$ -diazo nitrate yields results similar to those obtained with the  $\beta$ -diazo-naphthalene sulphate, about 26 *per cent.* is converted into the ethyl ether of  $\beta$ -naphthol and 7 *per cent.* into naphthalene. A small quantity of mononitro- and dinitro-naphthol are also formed at the same time.

The decomposition in water is similar in all cases, the result being a coloring matter, some tar, and a naphthol,  $\alpha$ - or  $\beta$ -according as the diazo compound is  $\alpha$ - or  $\beta$ -.

When the  $\beta$ -diazo-naphthalene sulphate is decomposed at ordinary temperatures by hydrochloric acid, about 50 *per cent.* is converted into  $\beta$ -chlor-naphthalene.

From the results obtained by Remsen<sup>1</sup> and his pupils the conclusion was reached that both the position and character of the groups or atoms in the molecule of the diazo compounds exert an influence on the decomposition of these compounds by alcohol. The work just recorded indicates that with diazo-naphthalene compounds, when the diazo group is in the  $\alpha$ -position, the tendency is toward the introduction of hydrogen when they are decomposed with alcohol, though both reactions take place simultaneously and the ethyl ether of  $\alpha$ -naphthol is formed as well as naphthalene, but in much smaller quantity. When, however, the diazo group is removed to the  $\beta$ -position, the reaction proceeds in exactly the reverse manner; the tendency here is towards the introduction of the ethoxy group in the place of the diazo group, though a small quantity of naphthalene is formed.

<sup>1</sup> This Journal 9, 387; 11, 319.

It is proposed to continue this study of the decomposition of the diazo compounds of naphthalene with alcohol, and to investigate the effect upon the reaction of the introduction of different groups in different positions in the molecule. Thus the 1:2  $\alpha$ -nitro-naphthyl amine will be converted into the diazo compound and decomposed with alcohol, and the 1:2  $\beta$ -nitro-naphthyl amine will be treated in the same way. The results will be compared, and thus it is hoped the influence of the nitro group may be determined.

CORNELL UNIVERSITY, *October, 1890.*

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Contributions from the Chemical Laboratory of Harvard College.

## LXXII.—THE REACTIONS OF SODIC ALCOHOLATES WITH TRIBROM-DINITRO-BENZENE AND TRIBROM-TRINITRO-BENZENE.<sup>1</sup>

BY C. LORING JACKSON AND W. H. WARREN.

We were induced to take up this piece of work—although at first sight it might seem to promise little of interest, either in the new compounds formed or in the nature of the reaction—by some experiments in a previous research, which apparently indicated that one of the atoms of bromine in tribrom-dinitro-benzene would be replaced by hydrogen under the influence of sodic ethylate. If this were the case, the work would supply additional material on which to found an explanation of the substitution of bromine by hydrogen in the formation of brom-dinitro-phenyl-malonic ester and allied compounds, described in several previous papers<sup>2</sup> from this Laboratory. Not only has the promise of these experiments been fulfilled, but the work has surpassed in interest all that we expected of it, as it has shown that sodic alcoholates (under which name we class phenolates also) act on tribrom-dinitro-benzene and tribrom-trinitro-benzene in four different ways:

<sup>1</sup> Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

<sup>2</sup> This Journal 11, 93; 12, 7, 164, 289, 307 (1889-90).

*First.* A simple replacement of each atom of bromine by the radicle of the alcoholate. This we have observed only in a single case,—the action of sodic phenolate on tribrom-trinitro-benzene giving trinitro-phloroglucine triphenyl-ether,  $C_6(NO_2)_3(OC_6H_5)_3$ , melting-point,  $175^\circ$ .

*Second.* The replacement of two atoms of bromine by two of the radicle of the alcoholate, the third atom of bromine remaining unaltered. Under this head come the actions of sodic ethylate, in the cold, methylate (in part), and phenolate on tribrom-dinitro-benzene, giving  $C_6HBr(C_2H_5O)_2(NO_2)_2$ , melting-point,  $184^\circ$ ;  $C_6HBr(CH_3O)_2(NO_2)_2$ , melting-point,  $237^\circ$ – $238^\circ$ ; and  $C_6HBr(C_6H_5O)_2(NO_2)_2$ , melting-point,  $165^\circ$ .

*Third.* The replacement of two atoms of bromine by the radicle of the alcoholate, and the third by hydrogen. Sodic ethylate when hot, and sodic methylate (in part) whether cold or hot, act in this way on tribrom-dinitro-benzene, giving  $C_6H_2(C_2H_5O)_2(NO_2)_2$ , melting-point,  $133^\circ$ ; and  $C_6H_2(CH_3O)_2(NO_2)_2$ , melting at  $167^\circ$ . These substances can also be made by boiling the corresponding bromine compounds (mentioned under the second class) with the proper alcoholate.

*Fourth.* The replacement of one, two, or perhaps three of the nitro groups by the radicle of the alcoholate, the three bromine atoms remaining unaffected. This very strange action was observed with sodic ethylate or methylate and tribrom-trinitro-benzene, giving  $C_6Br_3C_2H_5O(NO_2)_2$ , melting-point,  $147^\circ$ ;  $C_6Br_3(C_2H_5O)_2(NO_2)$ , melting-point,  $101^\circ$ ; and  $C_6Br_3(CH_3O)_2(NO_2)$ , melting-point,  $126^\circ$ .

The product of further action of sodic ethylate, when hot, on tribrom-nitro-resorcin diethyl-ether has not yet been obtained in a state of purity, but we hope to be able to describe it in a later paper.

We have little to say in general about these different modes of action of the alcoholates, except to connect them with previous observations of a similar character, as we think that the number of facts established is still insufficient for the safe foundation of a theoretical explanation of these differences. We hope to continue the work, however, until such a foundation has been secured. The formation of the trinitro-phloroglucine triphenyl-ether (described under the first head) is analogous to the formation of trinitro-phenylene-dimalonic ester from the brom-trinitro-phenyl-



malonic ester,<sup>1</sup> since in the corresponding dinitro compounds the third atom of bromine cannot be replaced by the phenoxy (see second head) or malonic ester radicle, as the case may be, even under more powerful inducements than are needed to bring about this action with the trinitro compounds, thus furnishing another example of the loosening effect of the presence of a third nitro group upon the bromine. The stability of the third atom of bromine in the dinitro compound, so far as replacement by an alcoholate radicle is concerned, mentioned under the second head, is analogous to that of the third bromine atom in dinitro-bromophenyl-malonic<sup>2</sup> or acetacetic<sup>3</sup> ester in the corresponding dinitro-dibrom compound,<sup>4</sup> and to a less extent in the trinitro derivative;<sup>5</sup> while the replacement of bromine by hydrogen, mentioned under the third head, corresponds closely to the removal of the second atom of bromine from all these substances. In regard to the replacement of the nitro groups instead of the atoms of bromine by ethoxy or methoxy radicles, described under the fourth head, we can only say that the conditions were essentially the same as those under which the bromine in the dinitro compound was replaced, and that as yet we have no hint of an explanation for it, but hope that future experiments will throw some light on the cause of this strange behavior. We may here call attention to the fact, that the replacement of these nitro groups is in direct contradiction to Laubentheimer's rule,<sup>6</sup> that a nitro group is removed only when it is in the *ortho* position to another nitro group, since in the tribrom-trinitro-benzene the three nitro groups are in the *meta* position to each other. Whether this exception to Laubentheimer's rule is due to the fact that it does not apply to sodic ethylate, or to some cause peculiar to the tribrom-trinitro-benzene, must be determined by future experiment.

We also found that neither sodic acetate nor sodic picrate acted on tribrom-dinitro-benzene even at 100°, nor did sodic picrate act on tribrom-trinitro-benzene, which justifies the inference that decidedly acid radicles cannot be taken up by these molecules, which contain so many nitro groups. Also we have repeated the experiment on the action of malonic ester upon tribrom-dinitro-benzene and confirm the negative results previously obtained.<sup>7</sup>

The description of the experimental details of the research occupies the rest of the paper.

<sup>1</sup> This Journal 12, 20 (1890).

<sup>2</sup> Ibid. 11, 94.

<sup>3</sup> Ibid. 167.

<sup>4</sup> Ibid. 12, 296.

<sup>5</sup> Ibid. 9.

<sup>6</sup> Ber. d. chem. Ges. 9, 766 1828.

<sup>7</sup> This Journal 12, 309.



*Action of Sodic Ethylate on Tribrom-dinitro-benzene in the Cold.*

In order to study this action 20 grams of tribrom-dinitro-benzene (melting-point,  $192^{\circ}$ : made from symmetrical tribrom-benzene) dissolved in a mixture of 40 cc. of benzene and 90 cc. of absolute alcohol, were treated with an alcoholic solution of the sodic ethylate, made from 3.4 grams of sodium, which gave the proportion of three molecules of sodic ethylate to one of tribrom-dinitro-benzene. That a reaction took place was indicated by the appearance of a pale reddish-yellow color, which gradually increased in intensity to a dark brownish-red, but there was no perceptible evolution of heat. To give the reaction time to run to an end, the mixture was allowed to stand in a corked flask at ordinary temperatures for two or three days, and then was filtered to remove a considerable amount of solid matter which had separated, and the filtrate allowed to evaporate spontaneously. The solid remaining on the filter was washed with water to remove sodic bromide, the presence of which was proved by testing this wash-water with argentic nitrate after acidification with nitric acid, and the portion insoluble in water added to the main product when that had been brought to the same degree of purity. This main product was deposited from the filtrate by the spontaneous evaporation of the solvent, and after washing with water was purified by crystallisation from hot alcohol until it showed the constant melting-point  $184^{\circ}$ . It is worth mentioning that the earlier crystallisations yielded round woolly masses of fine needles, which were gradually converted, as the substance approached purity, into well formed prisms or plates, since this change in the crystalline habit furnishes a convenient indication of the comparative purity of the substance. The analyses of the substance dried at  $100^{\circ}$  gave the following results:

I. 0.2616 gram of the substance gave on combustion 0.3426 gram of carbonic dioxide and 0.0904 gram of water.

II. 0.2753 gram of the substance gave 21.9 cc. of nitrogen at a temperature of  $25^{\circ}$  and a pressure of 745.5 mm.

III. 0.1830 gram of the substance gave, according to the method of Carius, 0.1032 gram of argentic bromide.

	Calculated for $C_6HBr(C_2H_5O)_2(NO_2)_2$ .	I.	Found. II.	III.
Carbon	35.83	35.72	...	...
Hydrogen	3.28	3.84	...	...
Nitrogen	8.36	...	8.70	...
Bromine	23.89	...	...	24.00

There can be no doubt, therefore, that this substance, melting at  $184^{\circ}$ , is the brom-dinitro-resorcin diethyl-ether formed by the replacement of two atoms of bromine by two of the ethoxy radicles.

The yield of brom-dinitro-resorcin diethyl-ether is far from good, 20 grams of tribrom-dinitro-benzene giving in no instance more than 4.6 grams of this substance, instead of the 16.5 grams required if the whole of the tribrom-dinitro-benzene had been converted into it, that is, about 28 per cent.; and, in fact, the alcoholic mother-liquors from its purification yielded on evaporation a viscous residue in large quantity, our unsatisfactory work upon which will be described after the statement of the properties of the brom-dinitro-resorcin diethyl-ether. We may give here, however, the result of a determination of the amount of sodic bromide formed in the reaction. 5 grams of tribrom-dinitro-benzene were treated in the cold with the sodic ethylate from 0.9 gram of sodium, in the manner described above, and, after the reaction had come to an end, water was added, the benzene solution removed, and the water extracted three times with benzene, after which it was made up to a volume of 500 cc., and the amount of sodic bromide determined in 20 cc. of this solution; the weight thus obtained calculated on the whole solution gave the result given below as found. The calculated number is the amount of sodic bromide which would be formed if two of the atoms of bromine in the tribrom-dinitro-benzene had been removed.

	Calculated.	Found.
Sodic bromide	1.271 gram	1.194 gram

These results agree as closely as could be expected considering the unavoidable losses in extracting with benzene, and prove that in this case two of the atoms of bromine contained in the tribrom-dinitro-benzene were removed as bromide of sodium.

*Properties of Brom-dinitro-resorcin Diethyl-ether,*  
 $C_6HBr(C_2H_5O)_2(NO_2)_2$ .

The substance crystallises from alcohol in rather thick, flattened needles of a yellowish-white color, which may attain a length of 1 cm. and sometimes a breadth of 1 mm. The ends are usually square, but less often consist of two planes at a very obtuse angle to each other. The larger crystals seem to be made up of needles united longitudinally, since their ends are apt to be sharply

serrated, or even as much indented as the teeth of a comb. Crystallised from benzene, it formed long slender prisms, sometimes reaching a length of 2 cm., terminated by two planes at an acute angle to each other: these effloresced on exposure to the air. They showed, however, the same melting-point as the crystals obtained from alcohol, and when recrystallised from this solvent gave the plates with square ends described above; they probably contained benzene of crystallisation, which escaped before the temperature had risen to the melting-point of the substance. It melts at  $184^{\circ}$ ; and is not very soluble in alcohol even when hot, less so when cold; slightly soluble in methyl alcohol; nearly insoluble in cold water, very slightly soluble in hot; freely soluble in acetone; soluble in benzene or chloroform; slightly soluble in ether or glacial acetic acid; nearly insoluble in carbonic disulphide, and insoluble in ligroine. Alcohol, or alcohol with a little benzene, is the best solvent for it. Neither sulphuric, nitric, nor hydrochloric acid has any apparent action on it, whether cold or hot.

As has been already stated, the alcoholic mother-liquors from the crystallisation of the brom-dinitro-resorcin diethyl-ether yielded on evaporation a semi-liquid mass of most uninviting properties, in considerable quantity; but although we have given much time to the study of this product, we are unable to make any definite statement in regard to its nature, and have not thought it worth while to postpone the printing of this paper until we could overcome the difficulties in its purification, as it does not lie in the direct line of our research, the principal object of which has been reached by our work on the brom-dinitro-resorcin diethyl-ether and its derivatives. We think it well, however, to give a brief statement of our work on this secondary product, since we have succeeded in isolating a crystalline substance from this viscous mixture by a process of liquation, which we think will prove of value to those chemists who have similar mixtures to deal with. This viscous mass, after standing for some weeks, solidified, but even then was deposited from all its solutions in its original oily condition, and as therefore it could not be crystallised directly we proceeded as follows: Having found that about one quarter of it melted at  $50^{\circ}$ – $60^{\circ}$ , we placed it on several layers of filter paper in a dish heated to about  $70^{\circ}$  by means of a water-bath, and allowed it to stand at this temperature for several days, renewing the filter paper as it was necessary, and towards the end of the process

applying a gentle pressure. The less-fusible residue thus obtained could now be crystallised from alcohol, and yielded a small quantity of a substance melting near  $170^{\circ}$ , which we took to be impure brom-dinitro-resorcin diethyl-ether, but the amount was so small that we could not recrystallise it often enough to raise the melting-point to the proper temperature,  $184^{\circ}$ . The principal part of this less-fusible portion melted in the neighborhood of  $150^{\circ}$ , and proved to be a mixture which, to judge by the melting-point, was the same as an abnormal product occasionally obtained from the process for making brom-dinitro-resorcin diethyl-ether instead of that substance, although we could find no difference in the conditions of the process from those when it gave the normal result. We have not succeeded in separating this mixture into its components, as, after several unsuccessful experiments, the amount remaining at our disposal was too small to continue with any prospect of success the crystallisations, which seemed to purify it very slowly, as they had but little effect on the melting-point. Some analyses of the mixture showed that it contained less carbon and more bromine than brom-dinitro-resorcin diethyl-ether.

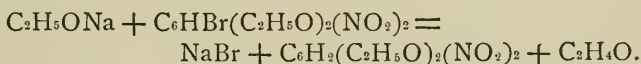
The more-fusible portion of the secondary product, which had been absorbed by the papers in the process of liquation, was extracted with alcohol, and the oil thus obtained allowed to stand until it had nearly solidified again, when it was submitted to a second liquation, the more-fusible product of which did not solidify, but only deposited a few crystals. As there were only about 10 grams of this in all, and it manifestly contained two, and, in all probability, three or more substances, we thought there would be little chance of isolating a pure compound from it, and accordingly, after one or two attempts to separate it into its components, its further study was abandoned.

*Action of Sodid Ethylate on Tribrom-dinitro-benzene with the Aid of Heat.*

As has been shown in the preceding section, sodic ethylate acting on tribrom-dinitro-benzene (melting-point,  $192^{\circ}$ ) in the cold converts it into brom-dinitro-resorcin diethyl-ether melting at  $184^{\circ}$ ; but if, instead, the two substances are heated together, a different product is obtained, which we have found it most convenient to prepare in the following way.—

A solution of 10 grams of tribrom-dinitro-benzene (melting-point,

192°) in 20 cc. of benzene was mixed with the alcoholic solution of sodic ethylate formed from 45 cc. of alcohol and 1.7 gram sodium, giving the proportion of three molecules of the ethylate to one of the tribrom-dinitro-benzene, and the mixture was heated on the steam-bath to gentle boiling for about ten minutes in a flask under a return-condenser. Longer or more violent heating should be avoided, as in this case a decomposition sets in, probably due to the action of the sodic ethylate on the nitro groups, which increases the difficulty in purifying the product. During the boiling the red color of the solution steadily increased in intensity, and a considerable amount of sodic bromide was deposited, together with a brown amorphous substance, which added to the turbidity of the reddish-brown liquid finally obtained. A curious odor was also observed in the solution, which seemed to be characteristic of all the reactions in which bromine was replaced by hydrogen, and was probably due to the secondary product formed from the sodic ethylate, but did not smell like the aldehyde which we had supposed would be this secondary product by the following reaction:



At the end of the ten minutes the solution was poured into an evaporating dish and allowed to evaporate to dryness spontaneously, washed with water to remove sodic bromide, and the reddish-brown substance insoluble in water, purified by crystallisation from alcohol with the aid of boneblack until it showed the constant melting-point 133°, when it was dried at 100°, and analysed with the results given under I and III. More than a year ago G. D. Moore, with one of us, obtained under somewhat different conditions the same substance, as shown by the melting-point and crystalline form, and we therefore add the analyses made of it by Dr. Moore at that time, II, IV and V.

I. 0.2200 gram of the substance gave on combustion 0.3752 gram of carbonic dioxide and 0.0950 gram of water.

II. 0.2320 gram of the substance gave 0.3990 gram of carbonic dioxide and 0.0995 gram of water.

III. 0.2112 gram of the substance gave 21 cc. of nitrogen at a temperature of 26° and a pressure of 754.8 mm.

IV. 0.2299 gram of the substance gave 22.3 cc. of nitrogen at a temperature of 23° and a pressure of 762.2 mm.



V. 0.2142 gram of the substance gave 20.3 cc. of nitrogen at a temperature of  $22.5^{\circ}$  and a pressure of 767 mm.

	Calculated for $C_6H_2(C_2H_5O)_2(NO_2)_2$ .	I.	II.	Found. III.	IV.	V.
Carbon	46.88	46.50	46.90	...	...	...
Hydrogen	4.69	4.80	4.77	...	...	...
Nitrogen	10.94	...	...	10.96	10.96	10.81

It contained no bromine.

These analyses prove that the substance is the dinitro-resorcin diethyl-ether, which must have been formed from the tribrom-dinitro-benzene  $C_6HBr_3(NO_2)_2$  by the replacement of two of its atoms of bromine by two ethoxy radicles ( $C_2H_5O$ ), the third by hydrogen, and we have here another case of the curious replacement of bromine by hydrogen in preference to its replacement by a radicle combined with sodium, which was first observed in the study of the action of sodium malonic ester upon tribrom-dinitro-benzene, and which induced us to undertake the present investigation. Since this dinitro-resorcin diethyl-ether melts at  $133^{\circ}$ , it is isomeric with the one<sup>1</sup> already known, melting at  $75^{\circ}$ .

*Properties of Dinitro-resorcin Diethyl-ether*,  $C_6H_2(C_2H_5O)_2(NO_2)_2$ .—This substance crystallises by cooling from an alcoholic solution in long, slender needles or flattened prisms with a sharp point. If the alcoholic solution is allowed to evaporate spontaneously, it forms some curling hair-like crystals which are very characteristic. The crystals from alcohol are also apt to form clumps of radiating hairs shaped somewhat like a toadstool, especially if the substance is not absolutely pure. From ether it crystallises in needles combined longitudinally into prisms with prickly ends; from chloroform, in radiating needles. It melts at  $133^{\circ}$ , and is nearly insoluble in water, although apparently a little more soluble in it hot than cold; not very soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; freely soluble in chloroform, glacial acetic acid, or acetone; soluble in benzene; slightly soluble in ether; very slightly in carbonic disulphide; essentially insoluble in ligroine. Alcohol is the best solvent for it. Strong sulphuric acid dissolves it in the cold, forming a yellow solution; strong nitric acid has no action on it when cold, but gives a colorless solution if heated with it; strong hydrochloric acid has no action on it, whether hot or cold.

<sup>1</sup>Aronheim: Ber. d. chem. Ges. 12, 32.



*Conversion of Brom-dinitro-resorcin Diethyl-ether into Dinitro-resorcin Diethyl-ether.*

It has been shown in the two preceding sections that the action of sodic ethylate on tribrom-dinitro-benzene differs according to the conditions under which it takes place, since in the cold brom-dinitro-resorcin diethyl-ether is formed, but when the mixture is heated the third atom of bromine is also removed and replaced by hydrogen, so that the product is the dinitro-resorcin diethyl-ether. In order to throw more light on this substitution of hydrogen for the third atom of bromine we next tried the action of sodic ethylate, when heated, on the brom-dinitro-resorcin diethyl-ether, as it was possible that this substitution could take place only at the moment of the replacement of the other two atoms of bromine by the ethoxy radicles, and in that case boiling sodic ethylate would not convert the ready-formed brom-dinitro-resorcin diethyl-ether into the dinitro-resorcin diethyl-ether. Accordingly 3 grams of brom-dinitro-resorcin diethyl-ether were mixed with the sodic ethylate from 0.6 gram sodium dissolved in alcohol,<sup>1</sup> and the mixture heated to gentle boiling for about ten minutes in a flask under a return-condenser, when it had taken on a dark-red color, and the curious odor observed in making the dinitro-resorcin diethyl-ether was very perceptible. The solvent was then allowed to evaporate spontaneously, and the residue washed with water, which removed sodic bromide (as was proved by the addition of argentic nitrate) and a red impurity. It was then purified by crystallisation from hot alcohol, until it showed a constant melting-point, when we found that this treatment had lowered the melting-point from 184°, that of the brom-dinitro-resorcin diethyl-ether, to 133°, that of the dinitro-resorcin diethyl-ether, which substance the product also resembled in appearance and solubility. To remove all doubt about its nature it was dried at 100° and analysed, with the following results:

0.1378 gram of the substance gave on combustion 0.2354 gram of carbonic dioxide and 0.0616 gram of water.

	Calculated for $C_6H_2(C_2H_5O)_2(NO_2)_2$ .	Found.
Carbon	46.88	46.58
Hydrogen	4.69	4.97

<sup>1</sup> We found that benzene must not be added in this case, as it seemed to interfere with the progress of the reaction.

This proves that the substance is the dinitro-resorcin diethyl-ether, and that the principal action of the hot sodic ethylate upon the brom-dinitro-resorcin diethyl-ether was the replacement of its bromine by hydrogen.

After the experiment just described had proved that the bromine in brom-dinitro-resorcin diethyl-ether could be replaced by hydrogen by means of boiling sodic ethylate, it seemed of interest to determine whether the same change could be brought about by other reagents, and we tried, first, alcohol alone, which might produce this action by giving aldehyde and hydrobromic acid as secondary products, although this was not at all probable, since the brom-dinitro-resorcin diethyl-ether was purified by crystallisation from hot alcohol; and indeed, after boiling it with alcohol for a long time in a flask under a return-condenser, the result was entirely negative, nothing but unaltered brom-dinitro-resorcin diethyl-ether, melting at  $184^{\circ}$ , being obtained on evaporation of the alcoholic solution.

From the action of malonic ester on brom-dinitro-resorcin diethyl-ether we expected better results, because, although it is true that malonic ester has no action on tribrom-dinitro-benzene,<sup>1</sup> in the formation of brom-dinitro-phenyl-malonic ester it seems to replace one atom of bromine by hydrogen in the dibrom-dinitro-phenyl-malonic ester<sup>2</sup> (which we must infer is an intermediate product in the reaction), and if this replacement is made possible by the presence of the malonic ester radicle  $\text{CH}(\text{COOC}_2\text{H}_5)_2$  in the molecule, we thought that perhaps the two ethoxy radicles in brom-dinitro-resorcin diethyl-ether might produce the same effect. The result of the experiment, however, was again negative, whether carried on cold or hot, as the solid product melted at  $184^{\circ}$ ; and the same result was obtained if acetacetic ester was used instead of malonic ester, although in this latter case the substances were boiled together for four hours.

Supposing from the negative results of these experiments that the presence of sodium malonic ester as well as malonic ester was necessary for the replacement of bromine by hydrogen in the hypothetical dibrom-dinitro-phenyl-malonic ester (leading to an immediate formation of acetylene-tetracarboxylic ester<sup>3</sup> as the secondary product), we tried the action of such a mixture, that is,

<sup>1</sup> See This Journal 12, 309, and the concluding section of this paper.

<sup>2</sup> This Journal 11, 547.

<sup>3</sup> Ibid. 12, 16.

one molecule of malonic ester to one molecule of sodium malonic ester, upon the brom-dinitro-resorcin diethyl-ether in alcoholic solution, at first in the cold for five days, that is, under the conditions used in the preparation of brom-dinitro-phenyl-malonic ester, but at the end of this time no sodic bromide could be detected, and essentially all the original ether was recovered unaltered. In another experiment the mixture was heated on the steam-bath for fifteen minutes, but, although a distinct red color appeared, the reaction could have been at best a very limited one, as essentially all the brom-dinitro-resorcin diethyl-ether was recovered unaltered, so that the new substance, if any were formed, was present in such small quantity that we were unable to detect it. It follows from these experiments, that the atom of bromine in brom-dinitro-resorcin diethyl-ether is more firmly attached to the molecule than the second atom of bromine in the hypothetical dibrom-dinitro-phenyl-malonic ester, since this is replaced by hydrogen through the agency of malonic and sodium malonic esters, or more probably by the malonic ester alone, considering the formation of tartronic acid.<sup>1</sup>

*Action of Sodid Methylate on Tribrom-dinitro-benzene.*

We took up this subject because it was possible that the action of sodic methylate might be different from that of sodic ethylate described in the preceding sections; but we have found that this is not the case, unfortunately at an expense of time and labor entirely out of proportion to the value of the results obtained.

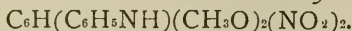
Our experience with sodic ethylate induced us at first to try the action of sodic methylate in the cold; but as we soon found that the same products were obtained when the action was assisted by heat, we have usually proceeded in this way, since, when boiling, the reaction runs to an end in ten minutes, whereas in the cold it takes about two days. Finally we adopted the following method: 10 grams of tribrom-dinitro-benzene dissolved in about 20 cc. of benzene were mixed with a solution in methyl alcohol of the sodic methylate from 1.7 gram of sodium, and the mixture boiled for ten minutes on the steam-bath in a flask fitted with a return-condenser, when a clear red solution was obtained, which on cooling deposited white crystals. These were filtered out, the filtrate allowed to evaporate to dryness, and the residue and

<sup>1</sup> This Journal **11**, 546.

crystals extracted three or four times with small amounts of hot alcohol, as in this way a viscous impurity was removed, the nature of which will be considered later. The purification of the less-soluble portion offered great difficulties, which was the more surprising because it was but slightly soluble in any solvent, so that the separation of it from the viscous product was very easy, and by crystallisation from hot alcohol we soon obtained a substance showing the constant melting-point  $237^{\circ}$ – $238^{\circ}$ ; but the results of its analysis did not agree with those calculated for brom-dinitro-resorcin dimethyl-ether, as is shown by the following comparison:

	Calculated for $C_6HBr(NO_2)_2(OCH_3)_2$ .	Found.
Carbon	31.27	32.78
Hydrogen	2.28	3.21
Nitrogen	9.12	10.64
Bromine	26.05	25.02

As these analyses seemed to indicate that the substance was not pure, we crystallised it again several times, using glacial acetic acid as the solvent; and after a new set of analyses had yielded no better results than those given above, we recrystallised six or seven times, this time from acetone, but with no better agreement of the percentages derived from analysis with those corresponding to the formula. As the substance crystallised very well, we were inclined to think at first that we had a compound different from the brom-dinitro-resorcin dimethyl-ether, probably with a higher molecular weight. Accordingly, we tried to determine the molecular weight of the substance by the method of Raoult, and obtained numbers not too far removed from the molecular weight of brom-dinitro-resorcin dimethyl-ether; but we do not think these results of any value, as the solubility of the substance in glacial acetic acid was so slight that the differences in the depression of the freezing-point for different molecular weights fell almost within the limits of error of the process. After many other experiments to determine the nature of this substance, which led to no result, we found at last in the anilido compound derived from it a body which could be purified by crystallisation, and from the analysis of which a safe inference could be drawn in regard to the nature of the substance melting at  $237^{\circ}$ – $238^{\circ}$ .

*Anilido-dinitro-resorcin Dimethyl-ether,*

This substance was prepared by heating the body melting at  $237^\circ$ – $238^\circ$ , with an excess of aniline at a temperature somewhat above  $100^\circ$  for about twelve hours, when the product was acidified with dilute sulphuric acid, washed carefully with water till all aniline salts were removed, and purified by crystallisation from hot alcohol until it showed the constant melting-point  $196^\circ$ . During this crystallisation we observed indications that we were dealing with a mixture, as the constant melting-point  $196^\circ$  was reached only when working with large quantities and after repeated crystallisation; but the impurity, which seemed to melt near  $206^\circ$ , was present in such small quantity that we were unable to determine its nature. The pure anilido compound was dried at  $100^\circ$ , and analysed with the following results:

I. 0.2973 gram of the substance gave on combustion 0.5733 gram of carbonic dioxide and 0.1167 gram of water.

II. 0.2064 gram of the substance gave 23.7 cc. of nitrogen at a temperature of  $22.5^\circ$  and a pressure of 761 mm.

	Calculated for $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NH})(\text{CH}_3\text{O})_2(\text{NO}_2)_2.$	I.	Found. II.
Carbon	52.66	52.59	...
Hydrogen	4.08	4.36	...
Nitrogen	13.16	...	13.02

From this it appears that the anilido compound is anilido-dinitro-resorcin dimethyl-ether, and consequently that the substance melting at  $237^\circ$ – $238^\circ$  must be essentially the brom-dinitro-resorcin dimethyl-ether, but that it contains some impurity which cannot be removed from it even by very long-continued crystallisation from alcohol, glacial acetic acid, or acetone; and this view is confirmed by the behavior of the anilido compound on crystallisation described above. Another determination of the nature of the substance melting at  $237^\circ$ – $238^\circ$  will be given below when we describe its conversion into dinitro-resorcin dimethyl-ether. The fact that in the action described above only the bromine was replaced by the aniline radicle  $\text{C}_6\text{H}_5\text{NH}$ , surprised us, as we had expected that the methoxy groups would undergo a similar replacement, owing to their position in regard to the nitro groups.



*Properties of Anilido-dinitro-resorcin Dimethyl-ether,*  
 $\text{C}_6\text{H}(\text{C}_6\text{H}_5\text{NH})(\text{CH}_3\text{O})_2(\text{NO}_2)_2$ .

This substance forms bright-yellow needles, or very slender prisms, which show some tendency to unite in radiating groups. It melts at  $196^\circ$ , and is nearly but not quite insoluble in water; not very soluble in cold ethyl or methyl alcohol, more soluble in hot; freely soluble in chloroform or acetone; soluble in benzene or glacial acetic acid; slightly in ether; very slightly in carbonic disulphide, and insoluble in ligroine. Alcohol is the best solvent for it.

*Properties of Brom-dinitro-resorcin Dimethyl-ether,*  
 $\text{C}_6\text{HBr}(\text{CH}_3\text{O})_2(\text{NO}_2)_2$ .

Although we did not succeed in getting this substance absolutely pure, we think it worth while to give its properties, as the slight amount of impurity present could have influenced them but little, and they differ rather strikingly from those of the corresponding ethyl compound. When crystallised from glacial acetic acid by cooling, it forms prisms terminated by a single rhombic plane at an acute angle to the sides of the prism, which are so short that the crystal looks almost like a rhombohedron; these crystals are white with a faint yellowish tinge, and often a millimeter long. When crystallised by slow evaporation of the glacial acetic acid solution, the crystals are converted into long, well-formed prisms, and the single rhombic plane which forms the principal termination is usually modified by other smaller planes. The highest melting-point which we have obtained for this substance was  $237^\circ$ – $238^\circ$ , but the analyses showed that even when melting at this point it was still far from pure. It is nearly insoluble in water, its solubility being perhaps somewhat increased by boiling; very slightly soluble in ethyl or methyl alcohol, the solubility somewhat increased by heat; slightly soluble in acetone, benzene, chloroform, glacial acetic acid, or nitrobenzene; very slightly in ether or carbonic disulphide; insoluble in ligroine. The best solvent for it is acetone or glacial acetic acid, as it is more soluble in these liquids than in any other; but its slight solubility in all the common solvents is one of its most striking properties.

*Dinitro-resorcin Dimethyl-ether*,  $C_6H_2(CH_3O)_2(NO_2)_2$ .

This substance was formed in addition to the brom-dinitro-resorcin dimethyl-ether by the action of sodic methylate in methyl alcoholic solution upon tribrom-dinitro-benzene, whether the substances were heated together, or the action was allowed to take place in the cold. The action of sodic methylate, therefore, on account of this indifference to the effect of temperature, is unlike that of sodic ethylate, which gave only brom-dinitro-resorcin diethyl-ether in the cold, and, when heated, only dinitro-resorcin diethyl-ether. The dinitro-resorcin dimethyl-ether, which was formed in comparatively small quantity, was obtained from the alcoholic washings and mother-liquors of the substance melting at  $237^{\circ}$ – $238^{\circ}$ . The residue left after the evaporation of the alcohol was a viscous mass, which contained, in addition to the substance of which we were in search, an oily impurity similar to that obtained from the ethyl compound, and a little brom-dinitro-resorcin dimethyl-ether. It was therefore a matter of some difficulty to isolate a pure substance from it, but we finally succeeded by repeated crystallisation from hot alcohol, during which crystals of two sorts were obtained, one consisting of white needles turning brown in the air, the other of lemon-yellow rhombic crystals, which appeared especially during the earlier parts of the crystallisation, and were gradually converted into the white needles. That the difference between the two forms consisted in the presence of one molecule of alcohol of crystallisation in the white needles was shown by the following analytical results:

I. 0.9817 gram of the air-dried substance lost 0.0177 gram at  $100^{\circ}$ .

II. 0.7617 gram of the substance dried *in vacuo* lost 0.0142 gram at  $100^{\circ}$ .

	Calculated for $C_6H_2(CH_3O)_2(NO_2)_2C_2H_5OH$ .	I.	Found.	II.
Alcohol	16.79	18.03		18.64

These numbers agree somewhat better with the percentages calculated for three molecules of water of crystallisation; but, apart from the improbability that the substance would take up water when crystallised from ordinary alcohol, we have found that the liquid given off, when the needles were heated in a test tube, dissolved the crystals clinging to the side of the tube, and that the substance dried at  $100^{\circ}$ , when recrystallised from absolute

alcohol, gave white prisms like those whose analysis is given above. The analysis which follows was made with the white needles after they had been dried at  $100^{\circ}$ , and therefore freed from their alcohol of crystallisation.

0.2688 gram of the substance gave on combustion 0.4092 gram of carbonic dioxide and 0.1027 gram of water.

	Calculated for $C_6H_2(CH_3O)_2(NO_2)_2$ .	Found.
Carbon	42.11	41.52
Hydrogen	3.51	4.25

The substance contains no bromine.

From these results it is evident that the substance is the dinitro-resorcin dimethyl-ether, but its melting-point,  $167^{\circ}$ , shows that it is isomeric with the substance<sup>1</sup> of this composition already known, which melts at  $67^{\circ}$ .

*Properties.*—The dinitro-resorcin dimethyl-ether was obtained crystallised with one molecule of alcohol, and also in crystals free from alcohol. When containing a molecule of alcohol it forms sheaves or bunches of white needles, or slender prisms often a centimeter long terminated by two planes at a very obtuse angle to each other, or, less often, a single plane at an acute angle to the sides; frequently also a single plane at right angles to the sides was observed, but we were inclined to consider this due to cleavage rather than a real termination of the crystal. These two prevailing forms, the two planes at an obtuse angle and the single plane at a right angle, give a general square-ended effect to the crystals which is characteristic. On exposure to the air these crystals turn purplish-brown. When containing no alcohol of crystallisation, it forms short, thick and broad crystals, apparently prisms of the monoclinic system, somewhat like certain feldspars, or rhombic crystals made up by the twinning of such prisms along one diagonal of the rhomb, and having a lemon-yellow color, which is not altered by exposure to the air. The melting-point is  $167^{\circ}$ , but the white needles melt a degree and a half below this point, probably on account of the presence of the vapor of alcohol. The substance is nearly insoluble in cold water, somewhat more soluble in hot; slightly soluble in cold ethyl or methyl alcohol, more soluble in hot; very freely soluble in acetone; freely in glacial acetic acid or benzene; soluble in chloroform; slightly

<sup>1</sup> Hönig: Ber. d. chem. Ges. **11**, 1041.

soluble in ether, less so in carbonic disulphide; and essentially insoluble in ligroine. The best solvent for it is boiling alcohol. The white needles, if recrystallised from chloroform or glacial acetic acid, give crystals of the lemon-yellow variety (that is, free from alcohol). Strong sulphuric acid in the cold has little, if any, action on it, when hot it dissolves a small quantity, forming a yellow solution; strong nitric acid does not dissolve it in the cold, but when hot dissolves it, forming a very pale-yellowish solution; strong hydrochloric acid has no action on it, either cold or hot.

The dinitro-resorcin dimethyl-ether was also made from the substance melting at  $237^{\circ}$ – $238^{\circ}$  (impure brom-dinitro-resorcin dimethyl-ether) by heating it to boiling with sodic methylate in methyl-alcohol solution for one hour in a flask with a return-condenser, at the end of which time the formation of dinitro-resorcin dimethyl-ether was proved by the melting-point,  $167^{\circ}$ , and the characteristic form of the crystals. This experiment shows that the action with the methyl compounds is similar to that with the ethyl compounds already described, but it takes place less easily, since in the ethyl series heating for ten minutes was sufficient to complete the action, whereas with the methylate boiling for an hour was necessary. This formation of dinitro-resorcin dimethyl-ether furnishes us with another and most convincing proof that the substance melting at  $237^{\circ}$ – $238^{\circ}$  is essentially brom-dinitro-resorcin dimethyl-ether, confirming our work with the anilido compound.

Some experiments on the action of sodic iso-amylate upon tribrom-dinitro-benzene gave under the conditions used with the ethylate and methylate only a viscous liquid, which did not solidify even after standing for two months, and as it did not distil with steam we decided that its purification would take more time than our interest in this subject would warrant, and accordingly abandoned this branch of the research.

#### *Action of Sodid Phenolate on Tribrom-dinitro-benzene.*

To study this action, 30 grams of tribrom-dinitro-benzene, dissolved in a mixture of alcohol and benzene, were mixed with an alcoholic solution of 20.8 grams of phenol previously converted into the sodium salt by the addition of a concentrated aqueous solution of 8.8 grams of sodic hydrate, and allowed to stand at ordinary temperatures over night. The amount of phenol used corres-

ponds to three molecules for every molecule of the tribrom-dinitro-benzene. The solution turned light-yellow, and deposited some crystals, apparently tribrom-dinitro-benzene, but the action was very limited, if any had taken place. Accordingly the mixture was heated on the steam-bath in a flask with a return-condenser for ten to twelve hours, when it turned dark-brown, and after the solvent had been distilled off there was left in the flask a brownish, viscous residue of the most uninviting appearance. This was thoroughly washed with water, and then allowed to stand for several days, which rendered it more solid; it was then washed three or four times with small quantities of cold alcohol, which removed much, but not by any means all, of the oily impurity, and the still-viscous residue recrystallised from a mixture of alcohol and benzene until it showed the constant melting-point  $165^{\circ}$ , when it was dried at  $100^{\circ}$ , and analysed with the following results:

I. 0.3128 gram of the substance gave on combustion 0.5781 gram of carbonic dioxide and 0.0790 gram of water.

II. 0.2051 gram of the substance gave according to the method of Carius 0.0888 gram of argentic bromide.

	Calculated for $C_6HBr(C_6H_5O)_2(NO_2)_2$ .	I.	Found. II.
Carbon	50.12	50.40	...
Hydrogen	2.55	2.81	...
Bromine	18.57	...	18.43

These results prove that the substance is the brom-dinitro-resorcin diphenyl-ether. We may add, that in one preparation, in addition to this a substance was obtained, crystallising in square plates and melting at about  $158^{\circ}$ , but in too small quantity for analysis, and we have not succeeded in making it again. We can say nothing about the nature of the oily product of the reaction, as we could find no way of purifying it.

*Properties of Brom-dinitro-resorcin Diphenyl-ether,*  
 $C_6HBr(C_6H_5O)_2(NO_2)_2$ .

This substance forms woolly masses of irregularly-radiating needles which under the microscope appear long and rather slender, with either a rounded sharpening at the point or else very sharp, tapering ends; the substance is white at first, but turns to a pale chocolate-brown on exposure to the air. It melts at  $165^{\circ}$ ,



and is very slightly soluble in water whether cold or hot ; slightly soluble in cold alcohol, more soluble in hot, but not freely ; rather more soluble in methyl than in ethyl alcohol, but not freely soluble even in this when hot ; very freely soluble in chloroform ; freely in benzene or acetone ; soluble in ether ; slightly soluble in glacial acetic acid or carbonic disulphide ; very slightly soluble in ligroine. The best solvent for it is a mixture of alcohol and benzene. Neither strong sulphuric nor hydrochloric acid seemed to have any action on it, hot or cold ; but strong nitric acid dissolved it after a few minutes' heating, and gave on dilution a new substance melting above  $200^{\circ}$ , probably a nitro compound. Sodid hydrate in solution has no perceptible action on the substance.

The removal of the bromine from the brom-dinitro-resorcin diphenyl-ether interested us especially, as the somewhat more acid nature of the phenol radicle ( $C_6H_5O$ ) would, we thought, exercise a marked influence on it ; unfortunately, however, the product has proved completely unmanageable, so that we can give only a very imperfect account of this action. We tried first hot sodid ethylate, but found that the substance was much more susceptible to its action than the corresponding ethyl or methyl compounds, showing signs of decomposition by turning dark when the mixture was heated for ten minutes ; and although a less-colored solution was obtained when we heated for only three or four minutes on the steam-bath, the residue left after spontaneous evaporation of the alcohol was a dark-colored, oily liquid which showed no signs of solidification, but gradually changed into a black tar after standing some months, and could not be brought into a state fit for analysis by any method we have been able to devise. The aqueous wash-water from this substance contained sodid bromide, so that there is no question that the bromine had been removed, but we are unable to determine whether it has been replaced by hydrogen or ethoxyl.

We thought it possible that the bromine might be removed from brom-dinitro-resorcin diphenyl-ether by phenol, tribrom-phenol being formed ; but after heating the substances together on the steam-bath for two days, essentially all the brom-dinitro-resorcin diphenyl-ether was recovered unaltered. A mixture of sodium malonic ester with an excess of malonic ester seemed to have more effect, as the liquid turned first pale yellow and then red. It was allowed to stand in the cold for several weeks, when it was found that a

small amount of sodic bromide had been formed; but the action was a very limited one, as almost all of the brom-dinitro-resorcin diphenyl-ether was recovered unaltered, and the new compound was present in such small quantity that we did not succeed in isolating it.

*Experiments with Tribrom-trinitro-benzene.*

After we had found that the bromine in brom-dinitro-resorcin diethyl-ether could be replaced with hydrogen by the action of hot sodic ethylate, it became interesting to find out whether this was the same atom of bromine which undergoes a similar replacement in making brom-dinitro-phenyl-malonic ester, that is, the atom which stands between the two nitro groups, and the easiest way to do this seemed to be to take up the study of the tribrom-trinitro-benzene, in which all the atoms of bromine are similarly placed. This we have done, but without the desired result, as the sodic alcoholates show with tribrom-trinitro-benzene actions entirely different from those with the corresponding dinitro compound.

*Action of Sodic Ethlyate on Tribrom-trinitro-benzene.*

To study this action 10 grams of tribrom-trinitro-benzene (symmetrical, melting at  $285^{\circ}$ ) were covered with ordinary alcohol in a flask, and to the mixture of crystals and alcohol 1.6 gram of sodium (three atoms of sodium would be a little over 1.5 gram) previously converted into sodic ethylate was added, in small portions at a time, the flask being immersed in cold water and shaken after each addition so as to avoid a rise of temperature<sup>1</sup> in any part of the liquid. The first drop of the alcoholic solution of sodic ethylate turned red on touching the liquid in the flask, and then faded to yellow; but as the remainder of the sodic ethylate was added, the color increased in intensity, until at last it had become a deep blood-red, while at the same time the undissolved solid began to diminish in quantity, and finally entirely disappeared, leaving a clear solution, thus showing that all the tribrom-trinitro-benzene had been used up, as it is nearly insoluble in alcohol. The mixture was allowed to stand over night, when it was found that a fresh amount of solid had been deposited: the solvent was then allowed to evaporate spontaneously, the residue (including the

<sup>1</sup> If the tribrom-trinitro-benzene was dissolved in benzene, the action was so violent that it was almost impossible to avoid a rise of temperature.

solid which had separated over night) washed with water until free from inorganic matter, and purified by crystallisation from alcohol until it showed the constant melting-point  $101^{\circ}$ , after which it was dried at about  $70^{\circ}$  and analysed, with the following unexpected results :

I. 0.3519 gram of the substance gave on combustion 0.3427 gram of carbonic dioxide and 0.0742 gram of water.

II. 0.2883 gram of the substance gave on combustion 0.2795 gram of carbonic dioxide and 0.0632 gram of water.

III. 0.3165 gram of the substance gave 9.8 cc. of nitrogen at a temperature of  $25^{\circ}$  and a pressure of 764.7 mm.

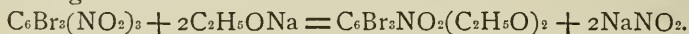
IV. 0.2315 gram of the substance gave by the method of Carius 0.2912 gram of argentic bromide.

V. 0.1588 gram of the substance gave 0.2002 gram of argentic bromide.

	Calculated for $C_6Br_3NO_2(C_2H_5O)_2$ .	I.	II.	Found. III.	IV.	V.
Carbon	26.79	26.56	26.43	...	...	...
Hydrogen	2.23	2.34	2.44	...	...	...
Nitrogen	3.13	...	...	3.48	...	...
Bromine	53.57	...	...	...	53.55	53.64

These results show that the action is entirely different from that with tribrom-dinitro-benzene, for this gave with sodic ethylate brom-dinitro-resorcin diethyl-ether,  $C_6HBr(OC_2H_5)_2(NO_2)_2$ , by the replacement of two atoms of bromine by two ethoxy radicles; whereas here, under the same conditions, we have the tribrom-nitro-resorcin diethyl-ether, which must have been formed by the replacement of two nitro groups by two ethoxy radicles. We have sought the confirmation of our analytical results, which their strangeness certainly requires, in the examination of the sodium salt formed in the reaction, which should be sodic nitrite instead of the sodic bromide which would have been formed if the reaction had run as it did with the dinitro compound. The aqueous washings from a new preparation of the substance melting at  $101^{\circ}$ , gave after acidification with nitric acid only a faint turbidity with argentic nitrate, showing that only a trace of sodic bromide had been formed, whereas from other portions of the wash-water we obtained the strongest reactions for a nitrite, as the following statement shows: Potassic iodide and starch-paste acidified with dilute sulphuric acid gave a very deep blue color; ferrous sul-

phate and sulphuric acid, a brownish-black color throughout the whole solution; a portion of the residue from evaporation of the wash-water added to strong sulphuric acid and phenol gave a reddish-brown color quickly passing through green to blue; strong sulphuric acid added to the residue from the evaporation of the wash-water gave off a gas recognised as nitrous fumes by the red color, and odor. There can be no doubt, therefore, that the sodic ethylate acts on tribrom-trinitro-benzene according to the following reaction:



We may add that, as we felt we could not be too careful in a case of this kind, the second specimen of tribrom-nitro-resorcin diethyl-ether was made from a quantity of tribrom-trinitro-benzene, the purity of which had been proved by analysis as well as by the melting-point—found: 53.60 per cent. of bromine instead of the 53.33 per cent. required by the formula.

As potassium compounds behave in many respects differently from the corresponding sodium compounds, we have repeated the experiment with potassic in place of sodic ethylate, but with the same result, that is, tribrom-nitro-resorcin diethyl-ether, melting at  $101^\circ$ , and potassic nitrite.

*Properties of Tribrom-nitro-resorcin Diethyl-ether,  $\text{C}_6\text{Br}_3\text{NO}_2(\text{OC}_2\text{H}_5)_2$ .*—This substance forms well-developed, white, flat prisms, usually with square ends, but sometimes terminated by two planes at an obtuse angle. It melts at  $101^\circ$ , and is very slightly if at all soluble in water, whether cold or hot; easily soluble in cold ethyl or methyl alcohol, still more freely in hot; very freely soluble in chloroform; freely in benzene; soluble in ether, acetone, carbonic disulphide, or glacial acetic acid; slightly soluble in ligroine. Hot alcohol is the best solvent for it. The three strong acids seem to have no action on it, whether they be hot or cold. Aniline dissolves it, but has no other action on it at ordinary temperatures, or even at  $150^\circ$ ; at higher temperatures a substance similar to rosaniline is formed. A mixture of malonic ester and sodium malonic ester was allowed to stand for several weeks with an alcoholic solution of this substance; but, although at the end of this time the liquid had assumed a slight reddish color, and a little sodic bromide (but no nitrite) had been formed, the action was so limited that the only organic compound which could be detected in the product was unaltered tribrom-nitro-resorcin

diethyl-ether, melting at  $101^{\circ}$ . It appears from these experiments that the tribrom-nitro-resorcin diethyl-ether is not an especially reactive substance, and yet when it was boiled with an alcoholic solution of sodic ethylate a reaction took place, as was shown by the dark color which the solution assumed, and the formation of a considerable amount of sodic nitrite, proved by the test with potassic iodide, starch, and dilute sulphuric acid. Unfortunately the end of the term prevented us from isolating the organic product, or, more probably, products, of this reaction, but the work will be continued next year.

*Tribrom-dinitro-phenetol*,  $C_6Br_3(NO_2)_2OC_2H_5$ .

In our first experiment on the action of sodic ethylate on tribrom-trinitro benzene the conditions were somewhat different from those described above, which gave us the tribrom-nitro-resorcin diethyl-ether, since benzene was used in addition to alcohol as a solvent, and no pains were taken to cool the liquid, although the reaction produced a noticeable amount of heat. The product, which was worked up by spontaneous evaporation of the solvent, washing, and recrystallisation from alcohol, showed the constant melting-point  $147^{\circ}$ , instead of  $101^{\circ}$ . Upon trying to make more of this substance in the same way, we obtained a product which was evidently a mixture of the substance melting at  $101^{\circ}$  and that melting at  $147^{\circ}$ , but the end of the term has prevented us from making out the exact conditions necessary for the production of the substance melting at  $147^{\circ}$  as the principal product. Fortunately the amount of this substance made in our first experiment was sufficient for its characterisation. It was dried at  $100^{\circ}$ , and analysed with the following results:

I. 0.1607 gram of the substance gave on combustion 0.1237 gram of carbonic dioxide and 0.0263 gram of water.

II. 0.2142 gram of the substance gave by the method of Carius 0.2683 gram of argentic bromide.

III. 0.1736 gram of the substance gave 0.2192 gram argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$ .	I.	Found. II.	III.
Carbon	21.38	20.99	...	...
Hydrogen	1.11	1.82	...	...
Bromine	53.46	...	53.31	53.74

*Properties.*—The tribrom-dinitro-phenetol occurs in white, well formed, slender, nearly-square prisms, often a centimeter long,



terminated by a single plane at an acute angle to the sides. It melts at  $147^{\circ}$ , and is soluble in cold ethyl or methyl alcohol, more freely in hot; freely soluble in benzene, chloroform, glacial acetic acid, or acetone; soluble in ether or carbonic disulphide; almost insoluble in ligroine. The best solvent for it is hot alcohol. None of the strong acids seem to have any action on it.

*Action of Sodid Methylate on Tribrom-trinitro-benzene.*

Since sodic ethylate had acted so abnormally with tribrom-trinitro-benzene, it seemed of interest to study the action of sodic methylate on this compound, and accordingly we proceeded as follows.

10 grams of tribrom-trinitro-benzene in a flask were covered with absolute methyl alcohol, and the solution of sodic methylate made from 1.5 gram of sodium was added, observing the precautions for keeping the mixture cool described under the preparation of the corresponding ethyl compound. The first drop of sodic methylate solution turned red on touching the liquid in the flask, but this color faded to yellow as it was diffused through the solution; with continued addition of the methylate the color increased in intensity, becoming finally blood-red. It seemed as if the action of the sodic methylate was more vigorous than that of the ethylate, as after about three quarters of an hour the whole of the tribrom-trinitro-benzene had disappeared, leaving a clear red solution, but nevertheless the mixture was allowed to stand over night to make certain that the reaction had come to an end, after which the solvent was evaporated spontaneously, the residue washed with water (which gave a test for sodic nitrite), and crystallised from hot alcohol until it showed the constant melting-point  $126^{\circ}$ , when it was dried at about  $70^{\circ}$ , and analysed with the following results:

I. 0.2856 gram of the substance gave 10.1 cc. of nitrogen at a temperature of  $25^{\circ}$  and a pressure of 755.5 mm.

II. 0.2295 gram of the substance gave by the method of Carius 0.3072 gram of argentic bromide.

III. 0.2311 gram of the substance gave 0.3096 gram of argentic bromide.

	Calculated for $C_6Br_3NO_2(CH_3O)_2$ .	I.	Found. II.	III.
Nitrogen	3.33	3.92	...	...
Bromine	57.15	...	56.97	57.03

*Properties of Tribrom-nitro-resorcin Dimethyl-ether*,  $C_6Br_3NO_2$   $(CH_3O)_2$ .—This substance crystallises in white, flattened prisms terminated usually by a single plane at a very sharp angle to the sides; rarely, by two planes at an obtuse angle to each other; or also, rarely, the ends are square. It melts at  $126^\circ$ ; and is nearly insoluble in cold water, perhaps a little more soluble in hot; only moderately soluble in ethyl alcohol even when hot, less soluble in it cold. It is much less soluble in alcohol than the corresponding ethyl compound; in this these two compounds resemble the methyl and ethyl compounds of the brom-dinitro-resorcin. Slightly soluble in cold methyl alcohol, more soluble in hot; freely soluble in benzene, chloroform, or acetone; soluble in ether, carbonic disulphide, or glacial acetic acid; very slightly soluble in ligroine. The three strong acids have no apparent action on it.

*Action of Sodid Phenolate on Tribrom-trinitro-benzene.*

After several unsuccessful experiments we obtained satisfactory results as follows: 10 grams of tribrom-trinitro-benzene were dissolved in a mixture of benzene and ordinary alcohol, and mixed with the sodid phenolate made from somewhat more than 6.1 grams of phenol treated with the sodid ethylate from 1.3 gram of sodium. The slight excess of phenol was used to avoid the presence of sodid ethylate, and the salt was added in suspension in alcohol. The mixture was then heated on the steam-bath under a return-condenser for less than five minutes, when it had turned bright green, but was perfectly clear, and upon cooling solidified, since it became filled with loose woolly masses of radiating needles looking like thistle-balls; this sudden solidification of the solution as it cools is very striking. The crystals with the residue from the mother-liquors were washed with water (which took up much sodid bromide), and crystallised from a mixture of alcohol and benzene until they showed the constant melting-point  $175^\circ$ , when they were dried at  $100^\circ$  and analysed. If benzene was not used in preparing this substance, the action was only incomplete, even after boiling for half an hour. The formation of sodid bromide instead of sodid nitrite, and the green instead of red color, showed that this action had gone differently from that with sodid ethylate or methylate, and this was confirmed by the following analyses:

I. 0.2689 gram of the substance gave on combustion 0.5823 gram of carbonic dioxide and 0.0850 gram of water.

II. 0.2439 gram of the substance gave 0.5306 gram of carbonic dioxide and 0.0775 gram of water.

III. 0.2448 gram of the substance gave 18.6 cc. of nitrogen at a temperature of 23° and a pressure of 758.1 mm.

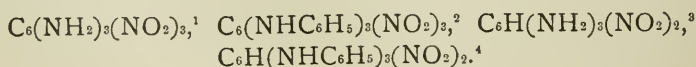
	Calculated for $C_6(C_6H_5O)_3(NO_2)_3$ .	I.	Found. II.	III.
Carbon	58.89	59.05	59.33	...
Hydrogen	3.07	3.51	3.53	...
Nitrogen	8.59	...	...	8.55

The substance was free from bromine. This action, therefore, has gone entirely differently from any of the others studied in this paper, consisting in the simple replacement of each bromine by one phenoxy radicle ( $C_6H_5O$ ), and the substance is the trinitro-phloroglucine triphenyl-ether.

*Properties of the Trinitro-phloroglucine Triphenyl-ether,*  
 $C_6(NO_2)_3(C_6H_5O)_3$ .

This substance crystallises in long, very slender, white needles, matted together into globular, woolly masses which turn olive-brown on exposure to the air. It melts at 175°, and is essentially insoluble in water, whether cold or hot; slightly soluble in cold alcohol, more soluble in hot, but not freely; its solubility in methyl alcohol is similar to that in ethyl alcohol; very freely soluble in acetone or chloroform; freely soluble in benzene or glacial acetic acid; slightly soluble in ether or carbonic disulphide; very slightly soluble in ligroine. The three strong acids have no apparent action on it, whether hot or cold.

This is the only case in which we have observed the replacement of all three of the atoms of bromine by the radicle of an alcoholate, and it is to be noted that the phenoxy radicle introduced here is the most acid one which we have succeeded in introducing, whereas in the other cases where all the bromine has been replaced by the same radicle this has been the alkaline amido or anilido group,



<sup>1</sup> This Journal 10, 237.

<sup>2</sup> Ibid. 290.

<sup>3</sup> Ibid. 11, 449.

<sup>4</sup> Ibid. 455.

*Experiments with Sodid Acetate, Sodid Picrate, or Sodid Nitro-methane on Tribrom-dinitro-benzene or Tribrom-trinitro-benzene.*

In order to study the action of more acid radicles upon tribrom-dinitro-benzene, we mixed 5 grams of it with 3 grams of sodic acetate dissolved in dilute alcohol, and, as there seemed to be no action in the cold, heated the mixture in a flask with a return-condenser on the steam-bath for eight hours, at the end of which time the tribrom-dinitro-benzene was recovered unaltered, as indicated by its melting-point,  $192^{\circ}$ . A similar mixture was next heated at  $100^{\circ}$  for two days in a soda-water bottle closed with an india-rubber stopper, at the end of which time 4.9 grams of tribrom-dinitro-benzene, melting at  $192^{\circ}$ , were recovered. It is evident from these experiments that sodic acetate has no action on tribrom-dinitro-benzene at  $100^{\circ}$ .

As we hoped that the slighter acidity of picric acid might allow it to react on tribrom-dinitro-benzene, although sodic acetate would not, we next allowed 6.3 grams of tribrom-dinitro-benzene to stand for a week with 12 grams of sodic picrate suspended in alcohol, and, as at the end of this time no sodic bromide had been formed, we heated it in a flask with a return-condenser on the steam-bath for two days, but even after this no sodic bromide could be detected, and 6.2 grams of tribrom-dinitro-benzene, melting at  $192^{\circ}$ , were recovered in place of the 6.3 grams used. Sodic picrate, therefore, does not act on tribrom-dinitro-benzene at  $100^{\circ}$ .

In the hope that tribrom-trinitro-benzene would prove more reactive than the dinitro compound in this case, as it has in many others, the experiment was repeated with this substance, 5 grams of tribrom-trinitro-benzene to 8.3 grams of sodic picrate mixed with alcohol and benzene being used, but after twelve hours' boiling the 5 grams of the trinitro compound were recovered unaltered.

The sodium salt of nitro-methane was also tried with tribrom-dinitro-benzene. 10 grams of the latter substance dissolved in alcohol and benzene were mixed with 4.5 grams of nitro-methane previously treated with the sodic ethylate from 1.8 gram of sodium. The mixture, after standing for some time in the cold, became brownish-red, and the sodium salt suspended in the solution gradually disappeared, but upon working up the product 9.5 grams of the tribrom-dinitro-benzene were recovered unaltered, showing that there had been no action worth considering. In a

previous experiment another compound was obtained in small quantity, but we are inclined to ascribe its formation to sodic ethylate, or the products of the decomposition of the sodium salt of nitro-methane rather than to that substance itself. We hope to return to this subject next year.

We had intended to include in this research the action of sodic hydrate in alcoholic solution upon tribrom-dinitro-benzene; but since we obtained from a preliminary experiment brom-dinitro-resorcin diethyl-ether, recognised by its melting-point ( $182^{\circ}$  instead of  $184^{\circ}$ , after one crystallisation) as the principal product, we thought the subject did not promise to be of sufficient interest to repay future work.

Some preliminary experiments with mononitro-tribrom-benzene and sodic ethylate seemed to promise interesting results, but this part of the work must be postponed until next year.

*Action of Malonic Ester on Tribrom-dinitro-benzene.*

In previous papers<sup>1</sup> of this series it has been proved that in the formation of brom-dinitro-phenyl-malonic ester from sodium malonic ester and tribrom-dinitro-benzene the bromine atom replaced by hydrogen stands between two nitro groups. In view of this fact, it seemed desirable to determine whether the ease with which this atom of bromine was removed by the action of malonic ester depended only on this position, and experiments were tried and described in a previous paper<sup>2</sup> which seemed to disprove this view. On returning to the subject, this point seemed to us of so much importance that we determined to repeat the experiment, especially as the conditions under which the malonic ester acted on the tribrom-dinitro-benzene in the earlier work were not exactly the same as those of the action of the sodium malonic ester in the preparation of brom-dinitro-phenyl-malonic ester; accordingly, in repeating the experiment as described below, we have reproduced these conditions as exactly as possible, except that malonic ester was used in place of sodium malonic ester.

To 4 grams of malonic ester dissolved in 30 cc. of absolute alcohol were added 5 grams of tribrom-dinitro-benzene dissolved in anhydrous benzene, and the mixture was allowed to stand in the cold for three or four days, at the end of which time, there being

<sup>1</sup> This Journal 11, 556; 12, 1.

<sup>2</sup> Ibid. 12, 309.



no signs that a reaction had taken place, the solvent was allowed to evaporate spontaneously, and the malonic ester mother-liquor poured off from the crystals, which, after careful drying on a steam radiator at about  $70^{\circ}$ , weighed 3.4 grams and melted at  $192^{\circ}$  (the melting-point of tribrom-dinitro-benzene). The mother-liquor was allowed to stand in a loosely covered dish for a month, when the malonic ester had evaporated, leaving an additional crop of crystals, which, after drying as before, weighed 1.75 gram, and also showed the melting-point of the tribrom-dinitro-benzene. So that the weight of the recovered tribrom-dinitro-benzene was 5.15 grams.<sup>1</sup> This experiment therefore confirms those previously tried,<sup>2</sup> and proves conclusively that malonic ester has no action upon tribrom-dinitro-benzene ( $\text{C}_6\text{BrNO}_2\text{BrNO}_2\text{BrH}$ ), and, consequently, that the replacement of the bromine atom by hydrogen in the formation of brom-dinitro-phenyl-malonic ester depends on other conditions in addition to the influence of the nitro groups and other bromine atoms upon it. The discussion of these other conditions will be postponed until we have collected more experimental material.

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## SOME DERIVATIVES OF PHTHALIC SULPHINIDE.<sup>3</sup>

By C. W. MOULTON.

Phthalic sulphinide was first obtained by Comstock,<sup>4</sup> and more carefully studied by Stokes,<sup>5</sup> who prepared several of its salts and ethers, and determined the constitution of its acid salts. The present work was undertaken with a view to studying the reactions involved in the preparation of this sulphinide and some of its derivatives.

The process employed was that recommended by Stokes, somewhat modified in certain details. It involves the following stages:

<sup>1</sup> The slight excess (0.15 gram) over the amount used is easily accounted for by the dust which during the long standing found its way into the loosely covered evaporating dish.

<sup>2</sup> This Journal 12, 309.

<sup>3</sup> It gives me great pleasure to acknowledge my indebtedness to Professor Remsen for his guidance and assistance in this work, which was undertaken at his suggestion and carried on under his immediate supervision.

<sup>4</sup> This Journal 5, 109.

<sup>5</sup> Ibid, 6, 262.

From naphthalene the  $\alpha$ -naphthalene-sulphonic acid is made, and converted successively into the sodium salt, the sulphon-chloride, and the sulphon-amide. The oxidation of the latter by potassium permanganate in alkaline solution yields the sulphinide. Since the quantity of the latter hitherto obtained had been but a small percentage of the theoretical yield, an attempt was made to determine what are the conditions most favorable for the best results at each stage of the process.

The results of the experiments upon the preparation of the sulphinide may be summed up in the following directions :

One kilogram of finely-powdered naphthalene is thoroughly rubbed up with 750 grams of sulphuric acid in the cold. It is then heated over a water-bath until the naphthalene melts, and is kept at this temperature, with constant stirring, for two hours. The whole is poured into 12 liters of water at  $85^{\circ}$ , allowed to cool to  $50^{\circ}$ , filtered through cloth, neutralised with chalk, again filtered through cloth, and the calcium precipitated with sodium carbonate. It is once more filtered through cloth and evaporated down to two liters. On cooling, the salt which separates will be a nearly-pure sodium  $\alpha$ -naphthalene-sulphonate. As much as possible of the mother-liquor is drawn off with a filter-pump, and the salt dried first at  $110^{\circ}$  and then at  $185^{\circ}$ , until water is no longer given off. The dry salt is powdered, and treated with 80 per cent. of its weight of phosphorus pentachloride, and, after heating on the water-bath to drive off the oxychloride, is cooled and washed once with cold water. The chloride is added in small portions to an excess of strong ammonia, and the mixture kept cool. The excess of ammonia is expelled by heating on the water-bath, and the sulphon-amide is washed by boiling in two or three liters of water, after which it is cooled, filtered out and dried. Of the amide, which is now sufficiently pure to oxidise, there should be about 450 grams. For the oxidation, 180 grams of crude caustic potash and 900 grams of potassium permanganate are dissolved in 12 liters of water, the solution heated to  $40^{\circ}$  and 200 grams of amide stirred in. The mixture is kept at a temperature between  $60^{\circ}$  and  $100^{\circ}$  until the permanganate is reduced; or for three hours, at the end of which time any remaining permanganate may be reduced with alcohol. After filtering through cloth and again through fluted filters, enough hydrochloric acid is added nearly to neutralise the alkali. The liquid is now evapo-

rated, *without boiling*, to one liter or less, and an excess of hydrochloric acid added, when upon cooling the acid potassium salt of the sulphinide separates out. This is dissolved in as much boiling water as may be necessary for solution, and recrystallised: a yield of 40-45 grams may be expected. Unless the manganese hydroxides are thoroughly washed, by boiling repeatedly in sufficient water, there will be a considerable loss, often more than 10 per cent. of the whole yield.

*Conversion of the Acid Potassium Salt into the Free Sulphinide.*

The salt thus obtained corresponded in appearance and properties with that described by Stokes. Since, according to this investigator, the potassium of this salt is acted upon very slowly by hydrochloric acid, he recommends the use of the silver salt from which to obtain the free sulphinide.

Upon boiling with *dilute* acid, however, more satisfactory results were obtained. 25 grams of crystallised acid potassium salt were dissolved in 450 cc. of water, and 50 cc. of concentrated hydrochloric acid (sp. gr., 1.175) added, and the whole boiled in a flask fitted with a reflux condenser. At the end of a half-hour the operation was suspended and the solution slowly evaporated to dryness. Upon recrystallisation from water, the product proved to be pure sulphinide, free from potassium chloride; but only 14 grams were obtained. To avoid so great a loss the experiment was repeated, as follows: 30 grams of the acid potassium salt were boiled with the same quantity of acid and water as before, for 15 minutes. The solution, treated as before, yielded 24 grams of sulphinide, and, as far as could be observed, was free from potassium chloride. When both the acid salt and the free sulphinide are present in a solution, if this be not too concentrated, on cooling, the much less soluble acid salt separates out first, although it may be subsequently obscured by the deposit of sulphinide. The crystalline form in which the acid salt first comes down from dilute solution is more characteristic than those described by Stokes. If the solution be of such a concentration that crystals begin to appear at about 50°, and the mother-liquor be poured off from the first-formed crystals while still hot, these crystals will appear at first sight to be steep rhombohedrons, but on closer examination more nearly resemble triclinic prisms terminated by basal planes. They are made up of thin plates parallel to the basal plane, and

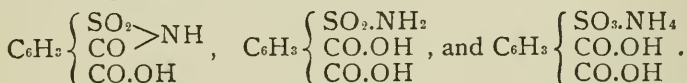
on account of this structure no satisfactory measurements could be obtained.

*Action of Hydrochloric Acid on Phthalic Sulphinide.*

Remsen and Burton<sup>1</sup> have shown that benzoic sulphinide, on being boiled with dilute hydrochloric acid, is converted first into sulphamine-benzoic acid, and finally into the acid ammonium salt of sulpho-benzoic acid. Regarded as successive steps in hydration, these compounds are represented thus:



By analogy we should expect the same changes to take place in phthalic sulphinide, giving successively



In the preparation of phthalic sulphinide, as described above, the loss due to boiling indicating that similar decomposition does take place, experiments were conducted with a view to obtain, if possible, the corresponding sulphamine acid and the acid ammonium salt of sulpho-phthalic acid.

5 grams sulphinide in 250 cc. hydrochloric acid, diluted as above, were boiled for two hours in a flask fitted with a reflux condenser. The solution was evaporated to about 50 cc., and, upon cooling, the greater part of the sulphinide was deposited unchanged. After filtering, the mother-liquors stood for 48 hours and deposited, together with more sulphinide, some well-formed crystals which may have been the sulphamine acid; they were not obtained, however, in large enough quantity for purification and analysis. These crystals were prismatic in habit, short and thick, for the most part terminated by the basal plane only. The basal section was nearly hexagonal, apparently from a nearly equal development of the orthorhombic prism and macropinacoid.

From subsequent experiments with proportions similar to those given above, it was found that after ten hours' boiling the sulphinide is completely changed and the final product of the reaction is reached. That this was the acid ammonium salt of sulpho-phthalic acid could not be demonstrated by analysis. It is

<sup>1</sup> This Journal 11, 404.

exceedingly soluble and, even when crystallised from absolute alcohol, in which it is quite easily soluble, it retains some of its impurities, and no satisfactory analysis could be obtained. The following facts, however, render it highly probable that the substance at hand was the acid ammonium salt :

1st. A solution of the crystallised substance was boiled a short time with an excess of barium carbonate, and a barium salt obtained which corresponded to the neutral barium salt of  $\alpha$ -sulpho-phthalic acid as described by Comstock and again by Stokes. The salt, dried at  $285^{\circ}$  (the temperature applied by the latter investigator), gave upon analysis —

Calculated for $\left( \text{C}_6\text{H}_3 \left\{ \begin{smallmatrix} \text{SO}_3 \\ \text{CO}_2 \\ \text{CO}_2 \end{smallmatrix} \right\} \right)_2 \text{Ba}_3.$		Found.
Ba	45.85 per cent.	45.60 per cent.

2d. A solution of the substance in absolute alcohol saturated with dry hydrochloric acid gave no ether of the sulphamine acid.

3d. On warming with caustic alkali ammonia was given off.

The analogy with benzoic sulphinide, which yields an acid ammonium salt under the same circumstances, leads to the same conclusion.

#### *Action of Potassium Carbonate on Phthalic Sulphinide.*

In evaporating the alkaline solution of the sulphinide, the loss on boiling indicated a breaking down of the ring under these conditions. To determine this point 3 grams of sulphinide were boiled with 10 grams of potassium carbonate in 200 cc. of water in a flask connected with a reflux condenser. On acidifying the solution after 10 hours' boiling, some acid potassium salt separated out. Another similar experiment gave, after 20 hours' boiling, no evidence of sulphinide on acidifying. An attempt to determine how far the hydration had gone under these circumstances was defeated by the difficulty of dealing with the products in the presence of so much inorganic matter, since they are exceedingly soluble in water and insoluble in ether.

The foregoing experiments show very conclusively that during the oxidation and subsequent concentration of the sulphinide, some loss must be expected if the solution be heated to boiling.

#### *Ethers of $\alpha$ -Sulphamine-phthalic Acid.*

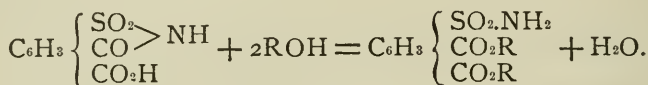
When benzoic sulphinide in solution in alcohol is treated with dry hydrochloric acid, the sulphinide ring breaks down and an



ether of sulphamine-benzoic acid is formed, according to the expression



In the case of phthalic sulphinide this reaction would be expected:



This is in fact the reaction which takes place under these conditions. Unless, however, the sulphinide be dry and absolute alcohol be used, and the whole boiled for some time after saturation with hydrochloric acid gas, the reaction is not complete. The acid potassium salt of the sulphinide, dried at  $185^\circ$ , gives the most satisfactory results in making these ethers. 10 grams, finely powdered and suspended in 100 cc. of an alcohol, may be converted into the corresponding ether in three hours. The dimethyl, di-ethyl and di-propyl ethers were thus prepared. Their crystallising power and stability diminish with the increasing complexity of the alcoholic residue.

#### *Di-methyl Ether of $\alpha$ -Sulphamine-phthalic Acid.*

This dissolves quite readily in hot water and, on cooling, crystallises in long, narrow, exceedingly thin plates, which show a tendency toward radial grouping. When dried upon the filter the mass shows a very characteristic pearly lustre. It is more stable than the corresponding ethyl ether. After the second recrystallisation it showed no further change in the melting-point, which is  $135^\circ$ . Analysis for nitrogen gave the following results:

Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{c} \text{SO}_2.\text{NH}_2 \\ \text{CO}_2.\text{CH}_3 \\ \text{CO}_2.\text{CH}_3 \end{array} \right\}$		Found.
N	5.14 per cent.	5.06 per cent.

Three determinations of sulphur made by Pearson's method gave, respectively, 10.76, 10.14 and 10.48 per cent., while theoretically there should be 11.74 per cent. of sulphur. In the last instance the greatest care was taken to secure complete oxidation, but apparently without success. Nevertheless it is not probable that the action with methyl alcohol differs from that with ethyl alcohol. The nitrogen analysis and the analogy with the ethyl

ether both point to the formula for this ether given above, while the wide divergence in these sulphur determinations tends to discredit them. A determination of the sulphur by Liebig's method gave the following results :

	Calculated for $C_6H_3 \left\{ \begin{array}{l} SO_2 \cdot NH_2 \\ CO_2 \cdot CH_3 \\ CO_2 \cdot CH_3 \end{array} \right.$	Found.
S	11.74 per cent.	11.89 per cent.

*Di-ethyl Ether of  $\alpha$ -Sulphamine-phthalic Acid.*

This dissolves in water much less easily than the corresponding di-methyl ether. From concentrated solutions it separates out, on cooling, as an emulsion, which on standing clears up with the formation of long, needle-shaped crystals arranged in small bundles, the individuals in each bundle lying parallel to one another. From less concentrated solutions it crystallises, directly on cooling, in a characteristic coral-like formation of crystals radially grouped, the extremity of each becoming a centre for another tuft of needles. Their melting-point is  $101.5^\circ$ – $102^\circ$ . Analysis of this ether gave the following results :

	Calculated for $C_6H_3 \left\{ \begin{array}{l} SO_2 \cdot NH_2 \\ CO_2 \cdot C_2H_5 \\ CO_2 \cdot C_2H_5 \end{array} \right.$	Found.
N	4.66 per cent.	4.58 per cent.
S	10.64     "	$\left\{ \begin{array}{l} 10.15 \text{ " } \\ 10.36 \text{ " } \end{array} \right.$

*Di-propyl Ether of  $\alpha$ -Sulphamine-phthalic Acid.*

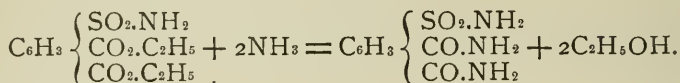
This ether was made in the same manner as the compound last described. It can be crystallised only with great difficulty, and then but in part, the remainder settling to the bottom as an oil. A quantity sufficient for analysis was not obtained in crystalline form. Although a number of attempts were made, crystals were obtained but twice. These showed melting-points of  $64^\circ$  and  $68^\circ$  respectively. I had reason to believe that the sample showing the higher melting-point was more nearly pure. The crystals were in no case well formed, and the crystallising power of the ether is very weak.

It is interesting to note that in these ethers the effect of the increasing complexity of the paraffin residue is to lower the melting-point, and by an approximately constant difference,—

Di-methyl ether,	. . . . .	135°
Di-ethyl ether,	. . . . .	102°
Di-propyl ether,	. . . . .	68°

*Action of Ammonia on the Di-ethyl Ether.*

From the action of ammonia upon ethereal salts in general we should expect the following reaction :



The ethyl ether was treated with an excess of strong ammonia in the cold, and allowed to stand 24 hours. It was then heated on the water-bath until no further odor of ammonia was given off, and, finally, was concentrated to a thin syrup, which on cooling was almost filled with crystals. These were recrystallised, and analysed for nitrogen with the following result :

Calculated for		Found.
$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2.\text{NH}_2 \\ \text{CO}.\text{NH}_2 \text{ or } \text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{N}.\text{NH}_4 \\ \text{CO}.\text{NH}_2 \end{array} \right. \end{array} \right.$		
N	17.32 per cent.	17.67 per cent.

Some of this crystallised product, dissolved in water and acidified, gave a precipitate of pure carbamine sulphinide.

*Carbamine Sulphinide.*

Carbamine sulphinide is somewhat more soluble in cold, and less in hot, water than the acid potassium salt of the sulphinide. It is slightly soluble in strong, boiling alcohol, and insoluble in ether. It melts at  $275^\circ$  (uncor.).

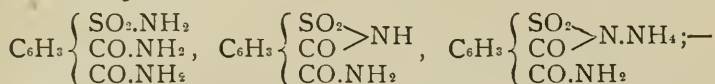
The crystals first formed in the hot solution, as described above in the case of the acid potassium salt of phthalic sulphinide, somewhat resemble those of the latter salt, but with apparently less inclination of the axes. The general habit of the crystals when allowed to grow undisturbed, is quite different from that of the acid potassium salt, and closely resembles that of benzoic sulphinide. The development is tabular and lozenge-shaped, with an irregular growth-line along the longer diagonal.

Analysis of the carbamine sulphinide gave the following results :

Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NH} \\ \text{CO} \\ \text{CO}.\text{NH}_2 \end{array} \right.$		Found.
N	12.42 per cent.	$\left\{ \begin{array}{l} 12.33 \text{ per cent.} \\ 12.15 \text{ " } \end{array} \right.$
S	14.17 "	14.38 "

Analysis of its salts confirmed these results.

Whether the ring was reformed by the action of the ammonia—the triamide losing one molecule of ammonia, and then taking it up again to form a salt; in which case the stages of the reaction would be represented thus:



or whether the action of the hydrochloric acid was necessary to reform the ring; was not determined. The former is the more probable supposition.

Three salts of the carbamine sulphinide were obtained:—

*Ammonium salt of carbamine sulphinide.*—The product of the action of ammonia upon the di-ethyl ether, as described above, was regarded as this ammonium salt—a conclusion drawn from the analysis and from the action of hydrochloric acid upon the compound. It is exceedingly soluble in water, from which it crystallises in fine, nearly-rectangular needles—apparently orthorhombic prisms terminated by dome faces of one form only.

*Barium salt of carbamine sulphinide.*—This separated as a crystalline precipitate, upon concentrating a solution of the carbamine sulphanide which had been boiled with barium carbonate. Its solubility in hot and in cold water were too nearly alike to render its purification by recrystallisation practicable with the small amount at hand. It was therefore dried to constant weight at 110°, and analysed for barium as follows:

	Found.
Ba	25.00 per cent.

From the following calculated values it will be seen that this corresponds more closely to the amount contained in the barium salt

of the monobasic acid  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NH} \\ \text{CO} \\ \text{CO}.\text{NH}_2 \end{array} \right. :$

	Calculated for		
$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{NBa}_{\frac{1}{2}} \\ \text{CO} \\ \text{CO}.\text{NH}_2 \end{array} \right. .$	$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2 > \text{N} > \text{Ba} \\ \text{CO}_2 \\ \text{CO}_2 \end{array} \right. .$	$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{SO}_2.\text{NH}_2 \\ \text{CO}_2 \\ \text{CO}_2 \end{array} \right\} \text{Ba} .$	
Ba	23.35 per cent.	37.87 per cent.	36.07 per cent.

*Silver salt of carbamine sulphinide.*—A hot, concentrated solution of carbamine sulphinide was treated with an excess of silver nitrate. Almost immediately a crystalline salt began to separate out. The crystals were not very sharply formed, but had a characteristic habit. Those especially which formed upon the side of

the beaker were 2 to 3 mm. in length, and appeared to be orthorhombic prisms terminated at both ends by steep brachydome faces so developed that the corresponding upper and lower planes nearly met. This salt is soluble in water only with great difficulty; 0.26 gram could not by prolonged boiling be brought completely into solution in a half-liter of water. The salt was analysed without recrystallising. Air-dried it gave 31.90 per cent. of silver; calculated for the silver salt of carbamine sulphinide, without water, 32.40 per cent.

As was afterwards shown, these unsatisfactory results were due to the fact that carbamine sulphinide is decomposed by boiling in water, yielding phthalic sulphinide. The presence of salts of the latter compound with those of carbamine sulphinide prepared as above, was therefore to be expected.

#### *$\alpha$ -Sulpho-phthalic Acid.*

Salts of this acid have been described by Comstock and by Stokes. The free acid has not before been prepared.

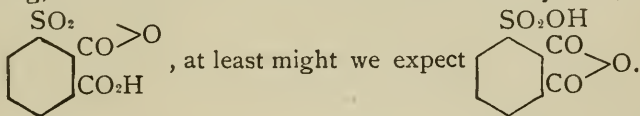
The acid ammonium salt described above, obtained by the action of dilute hydrochloric acid upon phthalic sulphinide, was mixed with an excess of phosphorus pentachloride. In most cases no action was perceptible until the mixture was quite strongly heated. The resulting chloride was washed in cold water. An attempt to crystallise this chloride failed. Some of the washed product, dried over phosphorus pentoxide and dissolved in absolute ether, remained as an oily mass after the evaporation of the ether. The chloride melts under water below the boiling-point, and is slowly decomposed by boiling water. It may be washed, with little loss, by boiling in water a short time. When boiled with water for two hours it is completely converted into the acid, which was identified by making the gelatinous silver salt described by Stokes, and also by the barium salt. It is extremely soluble in water, and quite easily soluble in absolute alcohol, but not at all in ether. If its aqueous solution be evaporated down to a thin syrup it becomes a solid mass of crystals when cold. By pouring off the mother-liquors before they were quite cold, crystals were obtained whose planes were not well formed, probably because of the rapidity of formation in so viscous a mass; for the substance has strong crystallising powers, and a drop of a somewhat more dilute solution leaves, upon evaporating, a bunch of radiating needles. The best formed crystals were apparently triclinic,



columnar in habit, with a development of the fundamental prism and macropinacoid, terminated by the basal plane. They melt in the water which clings to them, below  $35^{\circ}$ . Dried over night in a press between filter papers, they melt at  $62^{\circ}$ – $64^{\circ}$ . On standing exposed to the air for a few days they become opaque. An attempt to determine the water of crystallisation was unsatisfactory. Some of the acid, dried as above, was heated for 5 hours below  $100^{\circ}$ , but no constant weight was reached. It was then heated several hours longer below  $120^{\circ}$ , until the loss of weight nearly ceased, the loss being very slow during the last hour. The entire loss was 19.75 per cent. of the acid taken, corresponding more nearly to four molecules (22.64 per cent.) of water of crystallisation. Even below  $100^{\circ}$  the acid blackened somewhat; and when the operation was discontinued, was blackened nearly throughout. On attempting to redissolve in water, the greater part passed readily into solution, but enough black insoluble matter remained to indicate that a decomposition had taken place to some extent.

*Attempt to Prepare an Anhydride of Sulpho-phthalic Acid.*

Remsen and Dohme<sup>1</sup> have shown that ortho-sulpho-benzoic acid gives, when sublimed with phosphorus pentoxide, an anhydride which has the formula  $C_6H_4 \left\{ \begin{smallmatrix} SO_2 \\ CO \end{smallmatrix} > O \right.$ . The ease with which phthalic anhydride is obtained is well known. Since, then, in *o*-sulpho-phthalic acid both these relations are regarded as existing, we would look for the formation of an anhydride, if not



Some of the sulpho-phthalic acid, dried for a month over sulphuric acid, and having apparently lost all its water of crystallisation, was mixed with phosphorus pentoxide and heated by means of a sulphuric acid bath, in a small flask provided with a cooling tube. After several hours' heating at  $175^{\circ}$  there was no evidence of sublimation. A sand bath was substituted for the acid bath, and the heat gradually increased until the mass within was blackened, but no sublimate was obtained.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

<sup>1</sup> This Journal 11, 334.

## THE ACTION OF AN ALCOHOLIC SOLUTION OF SILVER NITRATE ON THE ETHYL ETHER OF PHENYL-DIBROM-PROPIONIC ACID.

BY LEONARD P. KINNICUTT AND GEORGE D. MOORE.

In a paper on the action of alcoholic solutions of silver nitrate on aromatic compounds containing bromine in the side-chain, it was shown that its action on the ethyl ether of phenyl-dibrom-propionic acid was to remove one half of the bromine.<sup>1</sup> The substance formed was not at that time isolated; this we have now done, and find that it is the ethyl ether of phenyl- $\alpha$ -brom- $\beta$ -nitro-propionic acid.

If the ethyl ether of phenyl-dibrom-propionic acid is dissolved in boiling alcohol, and silver nitrate dissolved in alcohol is added in amounts equalling one, two or three molecules, a precipitation of bromide of silver immediately takes place, and at the end of an hour, the solution being shaken from time to time, this precipitate settles, leaving a perfectly clear solution. The amount of silver bromide obtained, whether one, two or three molecules of silver nitrate were used, was that which would be given by the removal of one atom of bromine from the ether.

On pouring the clear alcoholic solution into water an oil separates out, which can be separated from the water by shaking with ether. The oil so obtained, after being dried over calcium chloride, gave on analysis an amount of bromine corresponding to that required by the ethyl ether of phenyl-monobrom-mononitro-propionic acid. Three separate preparations of the oil, using different amounts of silver nitrate, gave the following percentages of bromine: 26.32, 26.42, 26.46.

Theory for  $C_6H_5CHNO_2CHBrCOOC_2H_5$ , 26.48.

The oil is of a pale straw color, with a sweetish odor, soluble in alcohol and ether.

Distilled in vacuum, 20 mm., it begins to boil at 85°, hydrobromic acid being given off. The temperature slowly rises to 180°, at which point all the oil distills over. After washing the distillate to remove the hydrobromic acid, and redistilling in vacuum, 20 mm. pressure, the oil begins to boil at 75°, hydro-

<sup>1</sup> Kinnicutt and Sweetser: This Journal 6, 415.

bromic acid again being given off. About one fourth of the oil distills over between  $75^{\circ}$  and  $85^{\circ}$ , the temperature then rises rapidly to  $165^{\circ}$ , the main portion of the oil distilling between  $165^{\circ}$  and  $175^{\circ}$ . The portion of the oil distilling between  $75^{\circ}$  and  $85^{\circ}$  has the odor, the boiling-point, and reaction with ammonia of benzoic aldehyde. The oil distilling between  $165^{\circ}$  and  $175^{\circ}$  still contains both nitrogen and bromine. On oxidation the substance yields benzoic aldehyde, and on treatment with sodium hydrate the monobrom-cinnamic acid which melts at  $131^{\circ}$  is formed. These reactions indicate that the nitro group must have the  $\beta$  position.

On heating the substance for a long time with an excess of an alcoholic solution of silver nitrate, slow decomposition takes place. Fifteen grams of the substance were treated with fifteen grams of silver nitrate dissolved in alcohol, placed in a flask connected with an inverted cooler, and heated over a water-bath. At the end of ten hours one-half gram of silver bromide was precipitated; this amount gradually diminished till at the end of two weeks no further reaction seemed to take place. The oil that was thus obtained contained about 16 per cent. of bromine, and from its odor benzoic aldehyde seemed to be present.

A further study of the nitro compound, and also the study of the products formed by the action of silver nitrate on various paraffin as well as aromatic bromine compounds, is now being carried on in the laboratory.

Kinnicutt and Sweetser<sup>1</sup> have already shown that nitrate of silver easily removes all the bromine from phenyl- $\beta$ -brom-propionic acid, while it has no action on either of the two isomeric monobrom-cinnamic acids. This is easily explained by ascribing to these two acids the formula recently given to them by Erlenmeyer,<sup>2</sup> and we hope the results of further work with silver nitrate will show that the position of bromine atoms in the side-chain can be determined by the use of this reagent.

WORCESTER POLYTECHNIC INSTITUTE.

<sup>1</sup> This Journal 6, 416.

<sup>2</sup> Ber. d. chem. Gesell. 23, 3130.

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## THE ELECTROLYSIS OF METALLIC PHOSPHATES IN ACID SOLUTION.

BY EDGAR F. SMITH.

In a former article,<sup>1</sup> bearing the above title, I showed that copper and cadmium could be precipitated electrolytically from solutions of their phosphates. Their separation from each other was also noted, as well as the separation of the individual metals from iron, aluminium, chromium, zinc, nickel, and cobalt. Further, the separation of copper from manganese was shown to answer all practical requirements. The free phosphoric acid, present in the solution, prevented the deposition of the manganese as dioxide.

Since reporting this last separation I have found that cadmium can be separated from manganese electrolytically without any particular difficulty.

*Cadmium from Manganese.*

When I electrolysed the acid phosphates of copper and manganese, 10 cc. of phosphoric acid (sp. gr., 1.347) were present in the solution. The current employed gave 0.10 cc. OH gas per minute. In the presence of such a large excess of acid, cadmium was not precipitated by a current yielding 10 cc. OH gas per minute. It therefore became necessary to know just what quantity of free acid could be present in the solution and the cadmium be entirely deposited. The quantity of acid requisite for the retention of the manganese was of importance. Several trials led to the following conditions as being best suited for the complete separation of the metals under discussion:

1. 10 cc. cadmium sulphate solution ( $\equiv$  0.2399 gram cadmium), 10 cc. manganese sulphate solution ( $\equiv$  0.1000 gram manganese), 20 cc. disodium phosphate (sp. gr., 1.0358), 3 cc. phosphoric acid (sp. gr., 1.347), and 100 cc. water were electrolysed with a current liberating 10 cc. OH gas per minute. In twelve hours 0.2394 gram cadmium was precipitated. Not the slightest deposition of manganese dioxide was observed upon the anode.

2. In this trial the conditions were precisely the same as those given in 1. The deposit of cadmium metal weighed 0.2400 gram.

It will be noticed that the error in the results is fully within the limit. Cadmium was not detected in the filtrate.

<sup>1</sup> This Journal 12, 329.

The deposits in both experiments were very crystalline. Hot water was employed in washing the metal. The drying was done upon a warm iron plate. The current was invariably increased for about an hour before its final interruption. The acid liquid was siphoned off from the metallic deposit before the vessel in which the precipitation occurred was disconnected.

Some of the heavier metals were studied in the same manner as copper and cadmium. The results of this study are given below. They are new and have value for the student of electrolysis.

#### *Platinum.*

0.2590 gram of ammonio-platinum chloride was dissolved in water. To this solution I added 30 cc. disodium phosphate (sp. gr., 1.0358), 5 cc. phosphoric acid, and diluted with water to 150 cc. A current liberating 0.8 cc. OH gas per minute acted upon the solution for a period of ten hours. The precipitated platinum metal was quite adherent. It was washed with water and alcohol. It weighed 0.1140 gram. The calculated amount of platinum corresponding to the quantity of double salt used in the trial is 0.1144 gram. The error is therefore 0.0004 gram.

Two additional trials gave 0.1255 gram and 0.1263 gram metal. The required quantity of platinum was 0.1260 gram.

The filtrates from these deposits were not discolored upon the addition of hydrogen sulphide. The precipitated metal was deposited upon a copper-coated platinum surface.

A current best suited for the precipitation of 0.1-0.2 gram metallic platinum should give about 0.4 cc. oxyhydrogen gas per minute. If the current exceeds 0.7-0.8 cc. OH gas per minute, the platinum is apt to separate in a spongy condition, and when the current falls as low as 0.2 cc. OH gas per minute, the copper coating dissolves.

Platinum is deposited very rapidly from its acid phosphate solution by the current.

The conditions outlined above allow of the electrolytic separation of platinum from the metals of the third and fourth groups.

#### *Palladium.*

This metal, under the influence of the current, separates very rapidly from a solution containing free phosphoric acid. The deposition is also complete.



1. A solution containing 0.1825 gram palladium, 20 cc. disodium phosphate (sp. gr., 1.0358), 5 cc. phosphoric acid (sp. gr., 1.347), and 125 cc. of water was electrolysed with a current giving 0.7 cc. OH gas per minute. The deposited metal weighed 0.1817 gram. It was washed with hot water. The deposition was made upon a copper-coated platinum dish.

2. The conditions of experiment were analogous to those in 1. The precipitated platinum weighed 0.1830 gram.

In each instance the deposit of metal was compact and adherent. It resembled ordinary sheet palladium in appearance after it was dried.

The efforts made to separate palladium from cadmium, zinc and other metals were fruitless. The palladium was always fully precipitated, but it either carried down with it as much as three per cent. of the associated metal, or it separated in spongy, black masses. For the present the acid phosphate solution of palladium can only be recommended for electrolysis when other metals are not present with the palladium.

### *Gold.*

1. The solution contained 0.1338 gram gold, 20 cc. disodium phosphate (sp. gr., 1.038), and 3 cc. phosphoric acid (sp. gr., 1.347). Total dilution, 160 cc. Current, 0.8 cc. OH gas per minute. The metal was deposited upon copper. The deposit weighed 0.1335 gram. The filtrate was found free from gold.

The metallic deposit was quite adherent and compact. It was washed with hot water.

2. The conditions were similar to those just mentioned under 1. The gold deposit weighed 0.1339 gram.

Trials made for the purpose of separating gold from cadmium were not successful. The same behavior was observed here as with palladium and cadmium. The gold separated completely from the solution, but it either carried down cadmium or it separated in a spongy mass. This last occurrence was always noticed when the quantity of phosphoric acid was increased.

I failed to separate palladium from zinc, notwithstanding the conditions were repeatedly modified. With gold and zinc the separation proceeded without the least difficulty.

*Gold from Zinc.*

A solution of 150 cc. volume contained 0.1338 gram gold, 0.1500 gram zinc, 30 cc. disodium phosphate (sp. gr., 1.0358), and 3 cc. phosphoric acid. It was electrolysed with a current giving 0.6 cc. OH gas per minute. The gold deposit was compact, and readily washed with hot water. It was dried over a warm iron plate. It weighed 0.1338 gram. Zinc was not precipitated.

*Gold from Cobalt.*

The quantity of metallic gold present was the same as in the preceding separation. The metallic cobalt was 0.2300 gram. The conditions, in all other respects, were the same as in the separation of gold from zinc. The precipitated gold weighed 0.1338 gram.

The current employed in the experiments recorded in this communication was derived from the "crowfoot" cells of the ordinary form. The flat platinum spiral in connection with the anode of the battery was  $1\frac{3}{4}$  inches from the cathode dish, in which the depositions of metal were made. All the precipitations occurred at the ordinary temperature.

The electrolysis of zinc, nickel, cobalt and iron phosphates, in acid solution, has thus far not yielded very encouraging results. Strong currents seem necessary. Even then the deposition of the metals is rather slow.

UNIVERSITY OF PENNSYLVANIA, January 10, 1891.

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## REVIEWS AND REPORTS.

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### HYDRAZINE HYDRATE AND THE DIAMMONIUM HALOGEN SALTS.

Two years ago a paper by Curtius and Jay<sup>1</sup> announced the fact of the isolation of hydrazine. Another paper in the same series has recently appeared,<sup>2</sup> in this case by Curtius and Schulz,

<sup>1</sup> J. prakt. Chem. [2] 39, 27. An abstract of this paper will be found in This Journal 11, 142.

<sup>2</sup> J. prakt. Chem. [2] 42, 521.

which deals with the constitution of hydrazine hydrate and the hydrazine halogen salts.

From the sulphate,  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ , prepared as described in the former paper, hydrazine hydrate is obtained when the salt is heated in a silver distilling-apparatus with caustic potash. The distilled hydrate was analysed, one of the methods used being based upon the reaction which takes place when platinum chloride in acid solution is treated with this base,—platinous chloride is formed and nitrogen is given off:



The nitrogen was collected and measured in an apparatus designed for the purpose. The analyses show that the composition of the hydrate is to be represented by the formula  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ . Numerous molecular weight determinations were made both by the vapor-density methods of Hofmann and Victor Meyer, and by the method of Raoult. These show (1) that in aqueous solution the hydrate has the composition represented by the formula  $\text{N}_2\text{H}_4\cdot 2\text{H}_2\text{O}$ ; that at  $100^\circ$  and *in vacuo* the vapor density corresponds to a molecular weight of 50 ( $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O} = 50$ ); that at  $170^\circ$  under ordinary pressure the density is only one half as great—showing, apparently, complete dissociation into hydrazine and water; and that above  $170^\circ$  the density increases again, until at the temperature of the lead-bath it appears to correspond to a molecular weight of 100!

Some of the properties of the hydrate have already been given.<sup>1</sup> In addition the following may be of interest: It is hygroscopic and attracts carbon dioxide from the air. It mixes with water and with alcohol in all proportions, but not with ether, chloroform or benzene. It will solidify in a mixture of solid carbon dioxide and ether. The specific gravity of the substance is 1.03 at  $21^\circ$ ; its boiling-point is  $118.5^\circ$  under a pressure of 739.5 mm. It reacts in a marked manner with (red) litmus- and turmeric-paper.

As soon as the attempt is made to isolate hydrazine from the hydrate serious difficulties are at once encountered. If, for example, the hydrate is allowed to drop upon powdered barium oxide, great heat is generated, but, on raising the temperature for the purpose of distilling off the hydrazine, the *hydrate* passes over unchanged. Repeated distillation over barium oxide does, however, abstract a little of the water, and as a result the liquid fumes strongly in the air. Since at  $170^\circ$  there is apparently complete dissociation into water and hydrazine, some of the hydrate was heated to that temperature in the presence of barium oxide in a closed tube. On opening the tube, hydrazine escaped in the form of white fumes characterised by an intense odor. Further work will be done upon the base thus isolated.

<sup>1</sup> This Journal 11, 142.

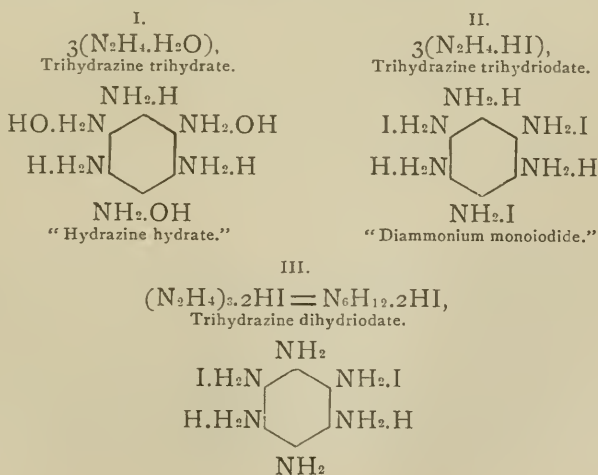
The following halogen salts are described:

- |      |   |  |  |   |
|------|---|--|--|---|
| I.   | $\text{N}_2\text{H}_4 \cdot 2\text{HF}$ , | $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$ , | $\text{N}_2\text{H}_4 \cdot 2\text{HBr}$ , | $\text{N}_2\text{H}_4 \cdot 2\text{HI}$ .     |
| II.  | ...                                       | $\text{N}_2\text{H}_4 \cdot \text{HCl}$ ,  | $\text{N}_2\text{H}_4 \cdot \text{HBr}$ ,  | $\text{N}_2\text{H}_4 \cdot \text{HI}$ .      |
| III. | ...                                       | ...  | ...  | $(\text{N}_2\text{H}_4)_3 \cdot 2\text{HI}$ . |

These salts exhibit in an interesting way the gradation in the properties of the halogen acids. For it will be seen that but one fluorine compound is known, and that the one containing the largest proportion of acid. Of the chlorine compounds, that belonging to the first class is prepared with ease by a number of methods; the second is obtained indirectly—by heating the more acid salt. Of the bromine compounds, that belonging to the second class is obtained with less difficulty than the other. Finally, of the hydriodic acid salts, the first is prepared only with considerable difficulty, the second—and *third*—with ease; no salt corresponding to the last but containing another halogen is known. Molecular weight determinations by Raoult's method were made for all these salts.

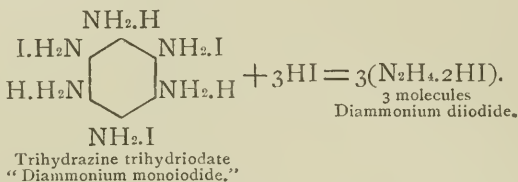
Among the reactions of these salts the following facts are to be noted: 1. The trihydrazine dihydriodate passes over with ease, on treatment with hydriodic acid, into "diammonium monoiodide"— $(\text{N}_2\text{H}_4)_3 \cdot 2\text{HI} + \text{HI} = 3(\text{N}_2\text{H}_4 \cdot \text{HI})$ ; and 2. It is only with considerable difficulty that this "monoiodide" can be transformed into the "diiodide,"  $\text{N}_2\text{H}_4 \cdot 2\text{HI}$ .

Taking these facts, together with the composition of the hydrate and salts, into consideration, the authors come to the conclusion that the only formulæ which will serve to represent the constitution of the derivatives of hydrazine belonging to the second and third classes, as given above, are of this kind:



The advantages attaching to the use of these formulæ are the following:

1. The formulæ are symmetrical.
2. The following transformations are easily understood:
  - a. The ready conversion of trihydrazine dihydriodate (Formula III) into "diammonium monoiodide" (Formula II).
  - b. The difficult transformation of the "diammonium monoiodide" into the diiodide. For in this case a breaking-down of the molecule must take place,—



3. The existence and stability of the mono-hydrate and the mono-halogen salts is easily explained; the formulæ represent saturated molecules.

WYATT W. RANDALL.

THE ELEMENTS OF QUALITATIVE ANALYSIS. By W. A. NOYES, Ph.D., Professor of Chemistry in the Rose Polytechnic Institute. Second Edition, revised. Holt & Co.: New York, 1890. 91 pp.

The author gives two reasons which have led to the writing of this book. "One has been the desire to give to my classes a scheme for qualitative analysis in which points where a beginner is liable to make mistakes are especially guarded by careful and explicit directions for procedure." "The second reason . . . has been the desire to connect the reactions given by way of a study of the elements before actual analysis more closely with the cause of analysis itself." Both reasons are good ones. The book shows that it has been prepared with unusual care by one well qualified for the work, and it can be recommended to those looking for a guide to qualitative analysis for use in large classes.

I. R.

ELECTRO-CHEMICAL ANALYSIS. By EDGAR F. SMITH, Professor of Analytical Chemistry, University of Pennsylvania. Blakiston, Son & Co., Philadelphia, 1890. 116 pp. 12mo.

Chemists will find this little book an excellent guide to a knowledge of the methods of quantitative analysis by electrolysis. As the author has himself contributed not a little to our knowledge of these methods, he is specially prepared for a work of this kind. The first part of the book treats of matters electrical,



such as Electrical Units, Sources of Electrical Currents, Reduction of the Current, Measuring Currents, etc. The special part then deals with the Determinations of Metals, Separation of Metals, and Oxidation by means of the Electric Current. In the case of each metal references are given to the original articles. The descriptions of the individual methods are sufficiently detailed to enable the student to follow them without difficulty. I. R.

ANLEITUNG ZUR DARSTELLUNG CHEMISCHER PRAEPARATE. Ein Leitfaden für den praktischen Unterricht in der unorganischen Chemie. Von Dr. HUGO ERDMANN. Frankfurt a. M.: Verlag von H. Bechholz. 1891.

This book aims to be for laboratory work in inorganic chemistry what the books of Fischer and Levy are for work in organic chemistry. It gives full directions for making nearly one hundred preparations, so chosen as to include derivatives of all the common elements. In the selection particular attention is given to the anhydrous chlorides, which, as the author says, test the ability of the student to work neatly and carefully. The author is Privatdocent at Halle, and has acted as laboratory assistant to Prof. Volhard for several years, during which time the methods here given were in constant use in the regular course of instruction, and were thoroughly tested. The book is good and really fills a gap in the list of laboratory handbooks. It can be recommended to students, and should certainly have a place in the library of every laboratory. E. R.

## NOTES.

### *Osmotic Pressure.*

In the *Zeitschr. f. Phys. Chem.* 6, 474, Prof. Boltzmann of Munich has a most interesting paper on osmotic pressure from a theoretical point of view. He considers the case of a dilute salt solution enclosed in a vessel with a "semi-permeable" diaphragm, and shows (*by simple mechanical principles*) that, when there is equilibrium, there must be a pressure exerted on the diaphragm, as a result of the actions of the salt-molecules and the solvent itself. If the temperature is the same, this pressure is identical with that which the same number of gaseous molecules occupying the same space as the solution would produce, provided only that

the mean kinetic energy of the two systems of particles is the same. The author discusses briefly cases of diffusion, electrolysis, etc., and by known laws and simple hypotheses arrives at the equations deduced by Arrhenius, Planck, Nernst and others.

J. S. AMES.

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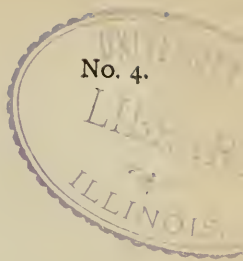
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# AMERICAN CHEMICAL JOURNAL.

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## INVESTIGATIONS ON THE SULPHINIDES.<sup>1</sup>

### VII.—ON SOME DERIVATIVES OF BENZOIC SULPHINIDE, AND THE CHANGES CAUSED IN THEIR TASTE BY CHANGES IN COMPOSITION.<sup>2</sup>

BY RUDOLF DE ROODE.

#### *Introduction.*

In a paper published in 1887, Remsen and Bayley<sup>3</sup> describe a method for the preparation of para-brom-sulphinide. Among its properties, the most characteristic is that it possesses two separate and distinct tastes, a sweet and a bitter. The substance was made the subject of an investigation by Drs. Howell and Kastle, of the Johns Hopkins University, and, in a paper entitled "On the Nerves of Taste," it was by them shown that the nerves in the tip of the tongue are of a different character from those in the back part, and that to the former the substance is only sweet, while to the latter it is only bitter.

Dr. Kastle prepared para-chlor-sulphinide, also, in order to ascertain whether it has a similar effect upon the nerves of taste or not. It was found to possess both tastes in a more marked degree than did para-brom-sulphinide.

The object of this research was to investigate the other parahalogen-sulphinides, and the substances from which they were

<sup>1</sup> The previous papers in this series have appeared in This Journal 6, 260; 8, 223; 9, 406.

<sup>2</sup> This investigation was undertaken at the suggestion of Professor Remsen, and I desire here to acknowledge my indebtedness to him for his valuable advice.

<sup>3</sup> This Journal 9, 229.



made, and to observe their effect upon the nerves of taste. It was thought that some definite relation might be found to exist between the intensity of the taste and the chemical nature of the halogen contained in the sulphinide. Since para-brom-sulphinide was both sweet and bitter, and para-chlor-sulphinide was more sweet and more bitter, it seemed probable that para-fluor-sulphinide would be still more sweet and still more bitter, while para-iodo-sulphinide would not be either as sweet or as bitter as the brom-sulphinide. We should thus have a series:

Para-fluor-sulphinide, intensely SWEET and BITTER.

Para-chlor-sulphinide, strongly SWEET and BITTER.

Para-brom-sulphinide, moderately Sweet and Bitter.

Para-iodo-sulphinide, slightly sweet and bitter.

As regards this point, however, it may be at once stated that no such definite relation was found to exist, for para-fluor-sulphinide was almost purely sweet—fully as sweet as benzoic sulphinide—with only a very slightly bitter after-taste, and para-iodo-sulphinide had very little taste at all, and that was purely bitter; so that the series ran thus:

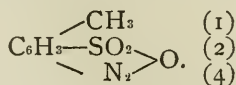
Para-fluor-sulphinide	=	SWEET	.	bitter.
“ chlor- “	=	SWEET	.	BITTER.
“ brom- “	=	Sweet	.	BITTER.
“ iodo- “	=	—	.	Bitter.

It therefore appears that no definite relation exists between the strength or chemical activity of the substituting halogen and the taste of the corresponding sulphinide.

The diazo compound which formed the starting-point in these investigations was made by starting with para-nitro-toluene, converting this into the ortho-sulphonic acid, which, by reduction with tin and hydrochloric acid, passes over into para-toluidine-ortho-sulphonic acid, from which the diazo compound was made.

*Para-diazo-toluene-ortho-sulphonic Acid.*

The starting-point in the preparation of the various compounds described in this paper was para-diazo-toluene-ortho-sulphonic acid<sup>1</sup> of the formula



<sup>1</sup>Ascher: Ann. Chem. (Liebig) **161**, 8.

This was made in the following manner: 50 grams of finely-powdered para-toluidine-ortho-sulphonic acid,<sup>1</sup> with 75 cc. of water, were made into a thin paste in a 500-cc. flask. The flask was placed in a bath of ice-water, and a rapid current of the gas from nitric acid and arsenic trioxide passed into it, the flask being constantly agitated. In from 10 to 15 minutes the contents of the flask had a frothy appearance, and granular crystals of the diazo compound had separated out. The current of gas was then stopped and the diazo compound almost completely precipitated as a heavy, granular mass, by the addition of about 300 cc. of alcohol. After agitating for a few minutes, this granular precipitate was rapidly filtered out with the aid of a pump, washed with alcohol, then with ether, and finally dried. In this manner, from 50 grams of para-toluidine-sulphonic acid 42 grams of pure-white diazo-toluene-sulphonic acid were obtained. On analysis—

I. 0.3973 gram gave 0.0555 gram nitrogen.

II. 0.3336 gram gave 0.0468 gram nitrogen.

	Calculated for $C_7H_6O_3N_2S$ .	I.	Found.	II.
N	14.14	13.97		14.03

*Para-fluor-toluene-ortho-sulphonic Acid.*

This acid was prepared by decomposing diazo-toluene-sulphonic acid with hydrofluoric acid in the following manner:

About 500 cc. of concentrated hydrofluoric acid were slightly warmed in a large platinum dish and 100 grams of the diazo compound dissolved in it, the solution taking place with ease. This solution was heated until decomposition, accompanied by evolution of nitrogen, began. This decomposition was allowed to take place slowly, and when complete, the contents of the dish were evaporated to a syrupy consistency, diluted with about two liters of water in a large porcelain dish, heated, neutralised with precipitated chalk, boiled with animal-charcoal, and filtered. The filtered solution gave a blue color with ferric chloride, owing to the fact that some of the diazo compound had been converted into para-cresol-sulphonic acid by the action of the water of the hydrofluoric acid solution. The calcium salt of the para-fluor-toluene-sulphonic acid was not obtained well crystallised and sufficiently pure for analysis. The barium salt, however (prepared

<sup>1</sup> Brackett and Hayes: This Journal 9, 400.

by neutralising with barium carbonate instead of precipitated chalk) was obtained in a very pure condition in small, glistening scales. It was recrystallised until its solution no longer gave a color with ferric chloride. When analysed—

I. 0.6160 gram, heated till constant weight, lost 0.0235 gram. 0.5925 gram dry salt gave 0.2704 gram  $\text{BaSO}_4$ .

II. 0.1090 gram, heated till constant weight, lost 0.0037 gram. 0.1053 gram dry salt gave 0.0477 gram  $\text{BaSO}_4$ .

	Calculated for $(\text{C}_7\text{H}_6\text{O}_3\text{SF})_2\text{Ba} + \text{H}_2\text{O}$ .	I.	Found.	II.
$\text{H}_2\text{O}$	3.38	3.81		3.40
Ba	26.60	26.83		26.63

As a qualitative test for fluorine, a small quantity of the salt was mixed with lime and ignited in a platinum crucible, or fused with caustic potash in a silver crucible; dissolved in hydrochloric acid (treated with a little calcium chloride if the caustic potash method had been used) and neutralised with ammonia. A precipitate of calcium fluoride was thus obtained, which, when treated with sulphuric acid, produced an etching on a watch-glass. One of these tests was employed in each of the cases where fluorine compounds were made, and fluorine was found to be present in each.

*Potassium fluor-toluene-sulphonate* was made from the barium or the calcium salt by treating with potassium carbonate. It crystallised from concentrated aqueous solution in large, glistening scales, very soluble in water. It may be precipitated as a granular powder by adding alcohol to the concentrated aqueous solution. The salt contains two molecules of water of crystallisation. On analysis—

I. 50 grams, heated till constant weight, lost 6.8545 grams. 0.6570 gram dry salt gave 0.2493 gram  $\text{K}_2\text{SO}_4$ .

II. 0.2019 gram, heated till constant weight, lost 0.0274 gram. 0.1745 gram dry salt gave 0.0669 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{C}_7\text{H}_6\text{O}_3\text{SFK} + 2\text{H}_2\text{O}$ .	I.	Found.	II.
$\text{H}_2\text{O}$	13.62	13.71		13.57
K	17.14	17.05		17.19

A qualitative test showed the presence of fluorine.

#### *Para-chlor-toluene-ortho-sulphonic Acid.*

This acid was prepared by decomposing diazo-toluene-sulphonic acid with hydrochloric acid, in the same way that the

fluor-toluene-sulphonic acid was made. Concentrated hydrochloric acid was used, and the product of decomposition was evaporated on the water-bath until very little odor of hydrochloric acid remained.

*Barium chlor-toluene-sulphonate* was made by diluting the syrupy residue with about three liters of water, neutralising with barium carbonate, boiling with animal-charcoal, filtering, and evaporating to crystallisation. The solution here, as in the case of the decomposition with hydrofluoric acid, gave a blue color with ferric chloride, due to the presence of the barium salt of paracresol-sulphonic acid. The barium salt of para-chlor-toluene-sulphonic acid separated out in wart-like, amorphous, granular aggregates. It was recrystallised until a solution of the salt no longer gave a color with ferric chloride. The salt is very little more soluble in hot than in cold water. It contains one molecule of water of crystallisation.

I. 0.2190 gram, heated till constant weight, lost 0.0070 gram.  
0.2120 gram dry salt gave 0.0528 gram  $\text{BaSO}_4$ .

II. 0.3714 gram, heated till constant weight, lost 0.0115 gram.  
0.3599 gram dry salt gave 0.0905 gram  $\text{BaSO}_4$ .

	Calculated for $(\text{C}_7\text{H}_6\text{O}_3\text{SCl})_2\text{Ba} + \text{H}_2\text{O}$ .	I.	Found. II.
$\text{H}_2\text{O}$	3.18	3.20	3.09
Ba	25.04	24.91	25.17

This salt is identical with that prepared by Jenssen,<sup>1</sup> and Hübner and Majert.<sup>2</sup>

*Potassium chlor-toluene-sulphonate* was made from the barium salt by treatment with potassium carbonate. It crystallises from concentrated aqueous solution in light-yellow needles without water of crystallisation.

I. 0.3191 gram gave 0.1139 gram  $\text{K}_2\text{SO}_4$ .

II. 0.2220 gram gave 0.0798 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{C}_7\text{H}_6\text{O}_3\text{SCK}$ .	I.	Found. II.
K	15.95	16.00	16.11

#### *Para-brom-toluene-ortho-sulphonic Acid.*

This acid was prepared by adding gradually 100 grams of diazo-toluene-sulphonic acid to 200 grams of warm, concentrated

<sup>1</sup>Ann. Chem. (Liebig) 172, 239.

<sup>2</sup>Ber. d. chem. Ges. 6, 793.

hydrobromic acid, and then heating till decomposition was complete.

*Barium brom-toluene-sulphonate* was prepared in the same manner as the corresponding chlor-toluene-sulphonate. It corresponded to the barium salt prepared by Jenssen,<sup>1</sup> and Hübner and Post.<sup>2</sup> The solution gave the color reaction with ferric chloride, showing that here also some cresol-sulphonic acid had been formed.

*Potassium brom-toluene-sulphonate* was made from the barium salt by treatment with potassium carbonate. This salt is not described by Hübner and Post.<sup>3</sup> It crystallises from the concentrated aqueous solution in thin, lustrous scales.

I. 0.2108 gram, heated till constant weight, lost 0.0122 gram.

II. 0.1986 gram dry salt gave 0.0598 gram  $K_2SO_4$ .

	Calculated for $C_7H_4O_3SBrK + H_2O$ .	Found.
H <sub>2</sub> O	5.86	5.79
K	13.50	13.50

#### *Para-iodo-toluene-ortho-sulphonic Acid.*

This acid was prepared by decomposing diazo-toluene-sulphonic acid with hydriodic acid in the following manner:

50 grams of the diazo compound were placed in a flask with 250 cc. of absolute alcohol, and 57 grams of concentrated hydriodic acid (57 per cent.) added in small portions, the flask being kept cool and being constantly agitated. When the evolution of nitrogen had ceased, the contents of the flask were gently warmed, in order to complete the decomposition, and the alcohol was then distilled off. The residue was diluted with five or six liters of water, heated, neutralised with lead oxide, and filtered while boiling-hot. The lead salt was very difficultly soluble, and could not be completely separated from the excess of lead oxide by repeated boiling with water. After being boiled two or three times with water, the residue was treated with a solution of potassium carbonate, which converted any undissolved lead salt into the potassium salt, which is easily soluble. The solution of the lead salt, upon cooling, becomes covered with an iridescent scum of a gummy consistency. If, however, the solution be evaporated to a small bulk, this scum gradually thickens as the boiling is continued, breaks up and

<sup>1</sup>Ann. Chem. (Liebig) 172, 237.

<sup>2</sup>Ibid. 169, 15.

<sup>3</sup>Ibid. 169, 7.



falls to the bottom in heavy flakes, which can easily be separated. The mother-liquor, upon further evaporation, yielded another lead salt, which was very soluble. These lead salts were not themselves further investigated, but were converted into the better-crystallised potassium salts by treatment with potassium carbonate.

*Potassium iodo-toluene-sulphonate* was obtained from the difficultly-soluble lead salt through treatment with potassium carbonate. It crystallised from moderately-concentrated aqueous solution in transparent, whetstone-shaped crystals, corresponding to those of the potassium salt of the  $\beta$ -iodo-toluene-sulphonic acid described by Glassner.<sup>1</sup> The salt contains iodine, as was proved by a qualitative test, and crystallises with one molecule of water of crystallisation.

I. 0.3260 gram, heated till constant weight, lost 0.0169 gram. 0.3091 gram dry salt gave 0.0791 gram  $K_2SO_4$ .

II. 0.3090 gram, heated till constant weight, lost 0.0159 gram. 0.2931 gram dry salt gave 0.0721 gram  $K_2SO_4$ .

	Calculated for $C_7H_6O_3SiK + H_2O$ .	Found.	
		I.	II.
H <sub>2</sub> O	5.08	5.18	5.14
K	11.61	11.11	11.03

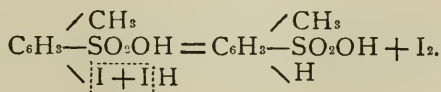
The other potassium salt was much more soluble, and crystallised from concentrated aqueous solution in thin flakes. It did not contain iodine, but on analysis gave figures corresponding to the potassium salt of toluene-sulphonic acid.<sup>2</sup>

I. 0.1687 gram, heated till constant weight, lost 0.0132 gram. 0.1555 gram dry salt gave 0.0631 gram  $K_2SO_4$ .

II. 0.2865 gram, heated to constant weight, lost 0.0221 gram. 0.2644 gram dry salt gave 0.1090 gram  $K_2SO_4$ .

	Calculated for $C_7H_7O_3SK + H_2O$ .	Found.	
		I.	II.
H <sub>2</sub> O	7.89	7.82	7.71
K	18.57	18.19	18.48

The toluene-sulphonic acid from which this salt was obtained was undoubtedly formed by the further action of hydriodic acid upon the para-iodo-toluene-sulphonic acid thus :



<sup>1</sup> Ber. d. chem. Ges. 8, 561.

<sup>2</sup> Terry: Ann. Chem. (Liebig) 169, 29.

The ease with which diazo-toluene-sulphonic acid is decomposed by the halogen acids increases as we pass from hydrofluoric to hydriodic acid.

The dry potassium salts of fluor-, chlor-, brom-, and iodo-toluene-sulphonic acids thus obtained, were treated, in turn, with phosphorus pentachloride and then with ammonia, thereby yielding the sulphon-chlorides and -amides. The details were as follows:

*Para-fluor-toluene-sulphon-amide.*

This was prepared by rubbing together in a dish 50 grams of anhydrous potassium fluor-toluene-sulphonate and 100 grams of phosphorus pentachloride; action taking place spontaneously and the mixture becoming hot and liquid. After driving off the greater part of the phosphorus oxychloride, and washing with cold water, the resulting sulphon-chloride, which was obtained as a slightly-yellow, viscous liquid, was allowed to drop slowly into a dish containing about a liter of strong aqueous ammonia. At first a bright-yellow solid was formed, which, after being broken up with a pestle and heated, went into solution. The solution was evaporated to dryness on the water-bath, the residue boiled with about 200 cc. of alcohol and a little animal-charcoal, filtered, and evaporated to crystallisation. The amide crystallises from the moderately-concentrated alcoholic solution in large, transparent, apparently orthorhombic, prisms terminated by dome-faces. It is easily soluble in alcohol and hot water, soluble with difficulty in cold water. From hot aqueous solution it crystallises in long, white needles. The melting-point is  $155^{\circ}$  (uncorrected).

I. 0.3137 gram gave 0.5093 gram  $\text{CO}_2$  and 0.1242 gram  $\text{H}_2\text{O}$ .<sup>1</sup>

II. 0.2505 gram gave 0.4071 gram  $\text{CO}_2$  and 0.0987 gram  $\text{H}_2\text{O}$ .

III. 0.5101 gram gave 0.0374 gram N (Kjeldahl).

IV. 0.1405 gram gave 0.1682 gram  $\text{BaSO}_4$  (Carius).<sup>2</sup>

V. 0.0895 gram gave 0.1123 gram  $\text{BaSO}_4$  (Carius).<sup>2</sup>

VI. 0.1053 gram gave 0.1306 gram  $\text{BaSO}_4$  (Pearson).<sup>2</sup>

VII. 0.1899 gram gave 0.2358 gram  $\text{BaSO}_4$  (Pearson).<sup>2</sup>

<sup>1</sup> The combustion-analyses of this, as well as those of the other compounds described in this paper, were made by a modified method devised by myself (*vide* This Journal **12**, 226). The method has been used with good results by several other students in this laboratory.

<sup>2</sup> These analyses were made by Mr. H. B. Skolfield, of the Johns Hopkins University.

	Calculated for $C_7H_8O_2NSF$ .	I.	II.	III.	Found. IV.	V. *	VI.	VII.
C	44.44	44.28	44.32	...	...	...	...	...
H	4.23	4.40	4.38	...	...	...	...	...
N	7.41	...	...	7.33	...	...	...	...
S	16.93	...	...	...	16.44	17.23	17.03	17.05
F	10.06	...	...	...	...	...	...	...
O	16.93	...	...	...	...	...	...	...

A qualitative test showed the presence of fluorine.

*Para-chlor-toluene-sulphon-amide.*

This was made in exactly the same manner as the fluor-toluene-sulphon-amide. It is easily soluble in alcohol and in hot water; soluble with difficulty in cold water. It does not crystallise well from alcoholic solution; from aqueous solution it crystallises, on cooling, in long, white needles. The melting-point is  $145^\circ$  (uncorrected). This amide corresponds to that of Heffter.<sup>1</sup>

I. 0.2819 gram gave 0.4210 gram  $CO_2$  and 0.1021 gram  $H_2O$ .

II. 0.3021 gram gave 0.4518 gram  $CO_2$  and 0.1077 gram  $H_2O$ .

III. 0.5161 gram gave 0.0356 gram N (Kjeldahl).

IV. 0.4901 gram gave 0.0337 gram N (Kjeldahl).

V. 0.4026 gram gave 0.4530 gram  $BaSO_4$  (Pearson).

VI. 0.2718 gram gave 0.3045 gram  $BaSO_4$  (Pearson).

VII. 0.3456 gram gave 0.2392 gram  $AgCl$  (burning with lime).

VIII. 0.4387 gram gave 0.3031 gram  $AgCl$  (burning with lime).

	Calculated for $C_7H_8O_2NSCl$ .	I.	II.	III.	Found. IV.	V.	VI.	VII.	VIII.
C	40.88	40.73	40.79	...	...	...	...	...	...
H	3.89	4.02	3.96	...	...	...	...	...	...
O	15.57	...	...	...	...	...	...	...	...
N	6.81	...	...	6.89	6.88	...	...	...	...
S	15.57	...	...	...	...	15.45	15.39	...	...
Cl	17.28	...	...	...	...	...	...	17.12	17.09

*Para-brom-toluene-sulphon-amide.*

This was made from potassium brom-toluene-sulphonate in the same manner as the corresponding fluor- and chlor- amides. This amide agreed with that prepared by Jenssen,<sup>2</sup> and Hübner and Post.<sup>3</sup>

<sup>1</sup>Ann. Chem. (Liebig) **221**, 209.

<sup>2</sup>Ibid. **172**, 238.

<sup>3</sup>Ibid. **169**, 15.

*Para-iodo-toluene-sulphon-amide.*

This was made by rubbing together in a dish 50 grams of anhydrous potassium iodo-toluene-sulphonate and 100 grams of phosphorus pentachloride. Action took place spontaneously, the mixture becoming hot and liquid. The resulting sulphon-chloride, after most of the phosphorus oxychloride had been driven off, was washed with cold water, and was thus obtained as a soft, white solid. When this was added to about a liter of strong aqueous ammonia, it did not all go into solution on boiling—as did the corresponding halogen compounds—but was nevertheless entirely converted into the amide. This amide is, therefore, not so soluble in ammonia as the others.

The contents of the dish were evaporated to dryness on the water-bath, boiled with about 200 cc. of alcohol and a little animal-charcoal, filtered, and evaporated to crystallisation. From the concentrated alcoholic solution the amide crystallises in fine, white needles. It is easily soluble in alcohol, sparingly soluble in hot water, from which on cooling it crystallises in white needles, finer than those from alcoholic solution. The melting-point is  $185^{\circ}$ – $187^{\circ}$  (uncorrected). This amide corresponds with the amide of the  $\beta$ -iodo-toluene-sulphonic acid prepared by Glassner.<sup>1</sup>

I. 0.1910 gram gave 0.2011 gram  $\text{CO}_2$  and 0.0566 gram  $\text{H}_2\text{O}$ .

II. 0.2200 gram gave 0.2243 gram  $\text{CO}_2$  and 0.0658 gram  $\text{H}_2\text{O}$ .

III. 0.5102 gram gave 0.02366 gram N (Kjeldahl).<sup>2</sup>

IV. 0.2080 gram gave 0.1641 gram AgI and 0.1640 gram  $\text{BaSO}_4$  (Carius).

V. 0.2539 gram gave 0.2006 gram AgI and 0.2003 gram  $\text{BaSO}_4$  (Carius).

	Calculated for $\text{C}_7\text{H}_5\text{O}_2\text{NSI}$ .	I.	II.	Found. III.	IV.	V.
C	28.28	28.71	27.80	...	...	...
H	2.69	3.29	3.32	...	...	...
O	10.78	...	...	...	...	...
N	4.71	...	...	4.64	...	...
S	10.78	...	...	...	10.82	10.83
I	42.76	...	...	...	42.64	42.70

*The Sulphinides.*

These sulphon-amides, when oxidised by means of an alkaline solution of potassium permanganate, yielded, respectively, fluor-,

<sup>1</sup> Ber. d. chem. Ges. 8, 561.

<sup>2</sup> This analysis was made by Mr. C. E. Saunders.

chlor-, brom-, and iodo-sulphinide. The percentage of sulphinide obtained was in all cases considerably less than the theoretical yield, although the oxidation was conducted under a variety of conditions. The conditions under which the best yield of sulphinide was obtained—and this, irrespective of the substituting halogen—were found to be the following:

First of all, the amide to be oxidised must be free from foreign substances, as a small amount of the impurities which are liable to occur in the preparation of the amide greatly affects the result.

20 grams of the amide and 8 grams of caustic potash are dissolved in two liters of water in a large flask. The flask is placed in a bath of boiling water, and a concentrated solution of 35 grams of potassium permanganate added, a little at a time. The flask is kept in the bath of boiling water until all of the permanganate has been added, and only a slight pink color remains. This requires, as a rule, from 6 to 8 hours. A little alcohol is then added and the contents of the flask filtered, after which the residue is washed with hot water and the filtrate evaporated to about 75 cc. While still warm, the sulphinide, together with some unoxidised amide, is precipitated by the addition of an excess of strong hydrochloric acid. When cold, the liquid is filtered with the aid of a pump, and the sulphinide and amide on the filter are washed with a little cold water. In order to separate the unoxidised amide from the sulphinide, the mixture is boiled with water, neutralised with precipitated chalk, filtered, and allowed to cool, when the amide crystallises out in long, white needles, and can be separated. The solution, on further evaporation, yields the calcium salt of the sulphinide. The calcium salts of para-fluor-, para-chlor-, para-brom-, and para-iodo-sulphinide all crystallise from concentrated aqueous solution in radial groups of white needles. These salts have the same tastes as the sulphinides themselves.

The following results were obtained on analysing the four calcium salts:

*Calcium Salt of Para-fluor-sulphinide.*

I. 0.1876 gram, heated till constant weight, lost 0.0439 gram. 0.1437 gram dry salt gave 0.0446 gram  $\text{CaSO}_4$ .

II. 0.2037 gram, heated till constant weight, lost 0.0476 gram. 0.1561 gram dry salt gave 0.0488 gram  $\text{CaSO}_4$ .



	Calculated for $(C_7H_3O_3NSF)_2Ca + 7\frac{1}{2}H_2O$ .	I.	Found.	II.
H <sub>2</sub> O	23.48	23.40		23.37
Ca	9.09	9.13		9.19

*Calcium Salt of Para-chlor-sulphinide.*

I. 0.2514 gram, heated till constant weight, lost 0.0560 gram.  
0.1954 gram dry salt gave 0.0553 gram CaSO<sub>4</sub>.

II. 0.2515 gram, heated till constant weight, lost 0.0561 gram.  
0.1954 gram dry salt gave 0.0565 gram CaSO<sub>4</sub>.

	Calculated for $(C_7H_3O_3NSCl)_2Ca + 7\frac{1}{2}H_2O$ .	I.	Found.	II.
H <sub>2</sub> O	22.20	22.27		22.31
Ca	8.46	8.32		8.50

*Calcium Salt of Para-brom-sulphinide.*

This salt was prepared by Remsen and Bayley.<sup>1</sup> It gave figures corresponding to the formula  $(C_7H_3O_3NSBr)_2Ca + 7\frac{1}{2}H_2O$ .

*Calcium Salt of Para-iodo-sulphinide.*

I. 0.2575 gram, heated till constant weight, lost 0.0439 gram.  
0.2136 gram dry salt gave 0.0440 gram CaSO<sub>4</sub>.

II. 0.2482 gram, heated till constant weight, lost 0.0422 gram.  
0.2060 gram dry salt gave 0.0421 gram CaSO<sub>4</sub>.

	Calculated for $(C_7H_3O_3NSI)_2Ca + 7\frac{1}{2}H_2O$ .	I.	Found.	II.
H <sub>2</sub> O	17.07	17.05		17.00
Ca	6.10	6.06		6.01

The sulphinides themselves were obtained as precipitates on adding hydrochloric acid to the saturated solutions of their respective calcium salts. They dissolve only with difficulty in cold water, and are even less soluble in hydrochloric acid.

*Para-fluor-sulphinide.*

This was obtained from its calcium salt by precipitation with hydrochloric acid, as stated above. It is moderately soluble in hot water, from which, on cooling, it crystallises in long, white needles which, on drying, break up into granules. When crystallised slowly from dilute solution it was obtained in small transparent rhombs. Its taste was almost purely sweet, but after

<sup>1</sup> This Journal 9, 232.

remaining in the mouth for a few minutes a slightly-bitter after-taste was perceptible. This is also the case with benzoic sulphinide itself. As nearly as could be judged, its sweetness was fully as great as that of benzoic sulphinide. Its melting-point was  $200^{\circ}$ – $202^{\circ}$  (uncorrected).

- I. 0.5086 gram gave 0.7772 gram  $\text{CO}_2$  and 0.0971 gram  $\text{H}_2\text{O}$ .
- II. 0.3980 gram gave 0.6080 gram  $\text{CO}_2$  and 0.0746 gram  $\text{H}_2\text{O}$ .
- III. 0.4873 gram gave 0.03346 gram nitrogen (Kjeldahl).
- IV. 0.5008 gram gave 0.0347 gram nitrogen (Kjeldahl).
- V. 0.3469 gram gave 0.3953 gram  $\text{BaSO}_4$  (Pearson).
- VI. 0.1856 gram gave 0.2096 gram  $\text{BaSO}_4$  (Pearson).

	Calculated for $\text{C}_7\text{H}_4\text{O}_3\text{NSF}$ .	I.	II.	III.	Found.	IV.	V.	VI.
C	41.79	41.68	41.66	...	...	...	...	...
H	1.99	2.12	2.08	...	...	...	...	...
O	23.88	...	...	...	...	...	...	...
N	6.97	...	...	6.87	6.93	...	...	...
S	15.92	...	...	...	...	15.65	15.51	...
F	9.45	...	...	...	...	...	...	...

A qualitative test proved the presence of fluorine.

#### *Para-chlor-sulphinide.*

This also was obtained from its calcium salt by precipitation with hydrochloric acid. It is not quite so soluble as para-fluor-sulphinide. It crystallises from aqueous solution in thin, pearly scales. The melting-point is  $218^{\circ}$  (uncorrected). It has both a sweet and a bitter taste. Both tastes are very marked, but the bitter seems to be the more intense of the two. This substance was prepared in small quantity by Dr. Kastle when at the Johns Hopkins University, in order to ascertain its effect upon the nerves of taste. It was not further studied by him, and its preparation was not put on record. I have obtained, on analysis, the following figures:

- I. 0.4416 gram gave 0.6234 gram  $\text{CO}_2$  and 0.0799 gram  $\text{H}_2\text{O}$ .
- II. 0.5671 gram gave 0.8021 gram  $\text{CO}_2$  and 0.0972 gram  $\text{H}_2\text{O}$ .
- III. 0.3125 gram gave 0.4414 gram  $\text{CO}_2$  and 0.0561 gram  $\text{H}_2\text{O}$ .
- IV. 1.0000 gram gave 61 cc. nitrogen at  $25^{\circ}$  and 738 mm. (Dumas).
- V. 1.0000 gram gave 60 cc. nitrogen at  $25^{\circ}$  and 736 mm. (Dumas).

VI. 1.0000 gram gave 60.6 cc. nitrogen at 25° and 734 mm. (Dumas).

VII. 0.7000 gram gave 0.04445 gram nitrogen (Kjeldahl).<sup>1</sup>

VIII. 0.7000 gram gave 0.0448 gram nitrogen (Kjeldahl).<sup>1</sup>

IX. 0.5113 gram gave 0.5497 gram BaSO<sub>4</sub> (Pearson).<sup>2</sup>

X. 0.3894 gram gave 0.4192 gram BaSO<sub>4</sub> (Pearson).<sup>2</sup>

XI. 1.0121 gram gave 0.6732 gram AgCl (burning with lime).

XII. 1.0006 gram gave 0.6603 gram AgCl (burning with lime).

XIII. 0.2141 gram gave 0.1414 gram AgCl (Carius).<sup>3</sup>

	Calculated for C <sub>7</sub> H <sub>4</sub> O <sub>3</sub> NSCl.	I.	II.	Found. III.	IV.	V.	VI.
C	38.62	38.50	38.57	38.52	...	...	...
H	1.84	2.01	1.90	1.99	...	...	...
O	22.07	...	...	...	...	...	...
N	6.44	...	...	...	6.60	6.47	6.52
S	14.71	...	...	...	...	...	...
Cl	16.32	...	...	...	...	...	...
	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
C	...	...	...	...	...	...	...
H	...	...	...	...	...	...	...
O	...	...	...	...	...	...	...
N	6.35	6.40	...	...	...	...	...
S	...	...	14.77	14.79	...	...	...
Cl	...	...	...	...	16.45	16.33	16.34

### *Para-brom-sulphinide.*

This was made from its calcium salt by precipitation with hydrochloric acid. It was slightly less soluble than para-chlor-sulphinide. Its properties corresponded in all respects with those of the substance prepared by Remsen and Bayley.<sup>4</sup> It possesses both tastes, but in a less marked degree than para-chlor-sulphinide. The yield obtained by conducting the oxidation of the sulphon-amide under the previously-mentioned conditions, was larger than was obtained by Remsen and Bayley. The yield was 10-12 per cent. of the theoretical.

<sup>1</sup> These analyses were made by Dr. A. M. Peter, Ky. Ag. Exp. Sta.

<sup>2</sup> These analyses were made by Dr. J. H. Holmes, J. H. U.

<sup>3</sup> This analysis was made by Mr. B. C. Hinde, J. H. U.

<sup>4</sup> This Journal 9, 229.

*Para-iodo-sulphinide.*

This, too, was obtained from its calcium salt by precipitation with hydrochloric acid. It is the least soluble of the halogen sulphinides. It crystallises from hot aqueous solution, on cooling, in fine, white needles. Its melting-point is  $230^{\circ}$ – $232^{\circ}$  (uncorrected). Its taste is not very marked, being only slightly bitter; there is no sweet taste whatever.

I. 0.3440 gram gave 0.3441 gram  $\text{CO}_2$  and 0.0414 gram  $\text{H}_2\text{O}$ .

II. 0.2624 gram gave 0.2632 gram  $\text{CO}_2$  and 0.0324 gram  $\text{H}_2\text{O}$ .

III. 0.2877 gram gave 0.2883 gram  $\text{CO}_2$  and 0.0361 gram  $\text{H}_2\text{O}$ .

IV. 0.6132 gram gave 0.0273 gram nitrogen (Kjeldahl).

V. 0.7017 gram gave 0.0309 gram nitrogen (Kjeldahl).

VI. 0.1819 gram gave 0.1390 gram  $\text{AgI}$  and 0.1387 gram  $\text{BaSO}_4$  (Carius).

VII. 0.2327 gram gave 0.1776 gram  $\text{AgI}$  and 0.1769 gram  $\text{BaSO}_4$  (Carius).

	Calculated for $\text{C}_7\text{H}_4\text{O}_3\text{NSI}$	I.	II.	III.	Found. IV.	V.	VI.	VII.
C	27.185	27.28	27.35	27.33	...	...	...	...
H	1.295	1.34	1.37	1.39	...	...	...	...
O	15.53	...	...	...	...	...	...	...
N	4.53	...	...	...	4.45	4.40	...	...
S	10.36	...	...	...	...	...	10.45	10.44
I	41.10	...	...	...	...	...	41.29	41.25

*Acid Ammonium Para-chlor-ortho-sulpho-benzoate.*

It is well known that, when boiled with dilute hydrochloric acid, benzoic sulphinide is converted into the acid ammonium salt of ortho-sulpho-benzoic acid.<sup>1</sup> It was thought very probable that under the same treatment the para-halogen-sulphinides would behave in the same manner. This was found to be the case with para-chlor-sulphinide. The other halogen sulphinides were not investigated with regard to this point. They would probably act in the same way.

5 grams of para-chlor-sulphinide were boiled with dilute hydrochloric acid for about an hour, the flask being connected with a reflux-condenser. The contents of the flask were then evaporated to dryness, and heated on the water-bath until all odor of hydro-

<sup>1</sup> Remsen and Burton: This Journal **11**, 404.

chloric acid had disappeared. The residue was dissolved in water, in which it was easily soluble. The solution had no taste, and on slow evaporation gave crystals similar in appearance to the acid ammonium salt of sulpho-benzoic acid. It was shown by analysis to be acid ammonium para-chlor-ortho-sulpho-benzoate.

I. 0.5372 gram gave 0.0359 gram  $\text{NH}_3$ .

II. 0.4896 gram gave 0.0321 gram  $\text{NH}_3$ .

		Calculated for	
		$\text{C}_6\text{H}_5-\text{SO}_2\text{O}.\text{NH}_4$	
		$\begin{array}{c} \text{COOH} \quad (1) \\ \diagup \\ \text{SO}_2\text{O}.\text{NH}_4 \quad (2) \\ \diagdown \\ \text{Cl} \quad (4) \end{array}$	
$\text{NH}_3$	6.71	I. Found.	II.
		6.68	6.56

While then the tastes of the halogen-derivatives of benzoic sulphinide differ markedly from one another, it is, as will be seen, a difficult matter to describe these differences accurately. The relative degrees of sweetness and bitterness can, of course, be only roughly measured. It is also impossible to make accurate comparison between a sweet and a bitter taste as regards the relative intensity of the two. There is also a difference of opinion amongst those who have tasted these substances. The majority, however, were of the opinion that the substances have the tastes described in the preceding pages.

## ON THE COMPOSITION OF CERTAIN PETROLEUM OILS, AND OF REFINING-RESIDUES.<sup>1</sup>

By CHARLES F. MABERY.

In an examination of crude Lima oil that I had occasion to make in the early development of the Ohio oil fields in 1885, I observed the peculiar, penetrating odor of the sulphur compounds; and while they were present in all fractions during distillation, I noted that they collected principally in the portions with higher boiling-points (between 200° and 300°). A systematic examination of the oil was soon undertaken for the purpose of ascertaining

<sup>1</sup> From the Proceedings of the American Academy of Arts and Sciences, Vol. 25 (December, 1890). Communicated by the Author.



the form of the sulphur compounds: but little had been accomplished when the work was interrupted by a destructive fire, and it was not resumed until two years later.

In published accounts of the composition of petroleum oils I have found very few allusions to the presence of sulphur, and those that appear are limited to the products of distillation. Hagar<sup>1</sup> found carbonic disulphide in petroleum-ether, but none in burning-oil. H. Vohl<sup>2</sup> reported sulphur in considerable quantities as sulphuric acid in numerous samples of crude (Roh) petroleum. But from the data given and allusions to the products as burning-oils, they had undoubtedly been refined with the aid of sulphuric acid. Much difficulty has been experienced in the removal of sulphur from the distillates of Ohio oil, and consequently few, if any, of the commercial products are entirely free from sulphur, while it is frequently present in considerable quantities.

This paper contains a description of results thus far obtained, of which the following is a summary:—

1. The separation and identification of methyl, ethyl, normal propyl, iso- and normal butyl, pentyl, ethyl-pentyl, and hexyl sulphides, which are present in crude Ohio petroleum.

2. The separation of certain sulphides that do not correspond in boiling-points nor in composition with any sulphides hitherto described: these will be further examined.

3. The separation of certain sulphur-free oils, apparently unsaturated, that also require further study.

I am not aware that these alkyl sulphides have hitherto been identified as natural products.

## I. THE SULPHUR COMPOUNDS IN OHIO PETROLEUM.

BY CHARLES F. MABERY AND ALBERT W. SMITH.

When the various distillates from Ohio oils are agitated with concentrated sulphuric acid, the sulphur compounds are partially removed in combination with the acid. By neutralising the acid solution with plumbic carbonate, filtering, and evaporating carefully, lead salts, soluble in water, are obtained that are easily decomposed by heat with the formation of plumbic sulphide. If the acid solution be neutralised with calcic carbonate or calcic hydrate,

<sup>1</sup> Jahresb. Liebig, 1867, p. 947, Aus. Pharm. Centrbl.

<sup>2</sup> Ibid., 1875, p. 1053; Dingl. Journal 216, 47.

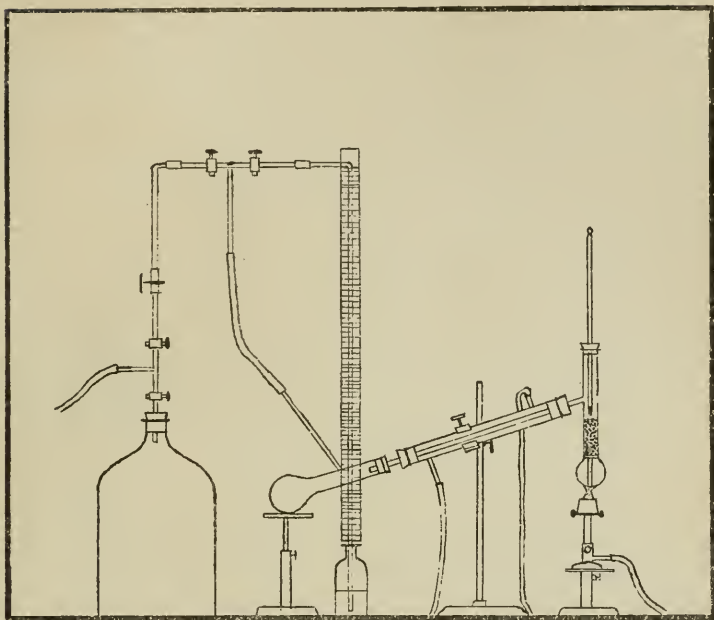
unstable calcium salts are formed that are readily decomposed by distillation with steam, which carries over the sulphides without decomposition.

In applying, for the separation of the sulphur compounds from the crude oil, a method based upon these observations, we procured fifty liters of what is technically known as sludge-acid, that had recently been used in refining Lima burning-oil, and, after dilution, we neutralised it in the cold with slaked lime and distilled the mixture of solution and solid with steam. We thus obtained 2270 grams of the sulphur-oil that was colorless when freshly distilled, and entirely free from hydric sulphide. Analysis showed that it contained 14.97 per cent. of sulphur with a specific gravity at 16.5° of 0.9245. Analyses of samples of crude Ohio oils from different localities have given on the average about 0.50 per cent. of sulphur.

Distillation of the oil with steam under atmospheric pressure produced such serious decomposition that we were forced to conduct all fractional separations with diminished pressure; but since the decomposition was inappreciable at tensions reduced to 150 mm., this involved but little additional labor, except in the inconvenience of maintaining the required tensions with the use of common corks without lutings, which became necessary on account of the solvent action of the oil. The fractional distillations were carried on in the apparatus represented in the accompanying diagram; while it contains no features not hitherto described, it may serve to illustrate how such an apparatus to work satisfactorily can readily be arranged from material always at hand in the laboratory.

Hill's<sup>1</sup> application of the Hempel device, which consists in supporting glass beads in the neck of the distillation-flask on a piece of glass rod with one end enlarged, is a means of saving much time in a long series of separations. The receiver is simply a second distillation-flask. This form of manometer was most convenient, since hydric sulphide was evolved to a certain extent, and, the manometer-tube becoming discolored by mercuric sulphide, occasionally it had to be cleaned. In exhausting the apparatus we used an ordinary glass water-pump, and to avoid loss of time in disconnecting the flask, a ten-liter bottle was inserted as a reservoir, with the stopcocks necessary for continuous action, and

<sup>1</sup> Proc. Am. Acad. 24, 342.



a nipper-tap with an enlarged thumbscrew was also attached for closely adjusting the pressure.<sup>1</sup> With this apparatus there is scarcely more interruption to continuous distillation than at atmospheric pressure. From 1000 grams of the oil at the end of the sixth distillation, with a tension of 150 mm., the following weights were obtained:

Temperatures,	-70°	70-80°	80-90°	90-95°	95-100°	100-105°
Grams,	12	8.5	16	16	26	20.5
Temperatures,	105-110°	110-115°	115-120°	120-125°	125-130°	130-135°
Grams,	31	30	83	47.5	59	66
Temperatures,	135-140°	140-145°	145-150°	150-155°	155-160°	160°+
Grams,	69	56.5	75	36	40.5	230
Total, . . . .						921.5

At the end of the twenty-second distillation, with the tension reduced to 100 mm., the products collected, to a large extent, within well-defined limits of temperature and several determinations of sulphur gave the following results:

<sup>1</sup> We were unable to use the convenient device of Anschütz for maintaining constant tensions, since the current of air produced considerable decomposition of the oils.

Fraction,	—76°	80-90°	98-101°	135-145°	148-155°	185-200°
Per cent. sulphur,	2.60	7.34	18.23	15.52	16.44	14.21

All fractions containing sulphur gave, with alcoholic, and with aqueous mercuric chloride, precipitates which were either crystalline, or, with the less-volatile products, thick, viscous oils. The latter usually became solid on standing, or when crystallised from benzene. As a qualitative test for sulphur, we depended upon the exceedingly delicate nitro-prussid reaction, which was especially serviceable in separating sulphur-oils from those containing no sulphur. The platinum compounds  $R_2SPtCl_4$  were readily formed with chlor-platinic acid with evolution of hydrochloric acid. With bromine all fractions united with great energy with the formation of oils heavier than water. These reactions suggested the presence of sulphides, or with sulphur-free oils the reaction with bromine indicated unsaturated hydrocarbons.

When distilled at temperatures above 140°, under atmospheric pressure, the oils became thick and dark in color, and hydric sulphide was freely evolved. Since at lower temperatures the decomposition was slight, the fractional separation of the products collected below 101° ( $P=100$  mm.—see above) was carried further. The products thus collected below 125°, united readily with concentrated hydrobromic acid when heated, forming oils heavier than water. The fraction 80°-90° was nearly all converted into the heavy addition-product, and the fraction 90°-100° separated into two products, one heavier and one lighter than water, the latter in somewhat smaller quantity than the former. The addition-product from the fraction 80°-90° possessed the characteristic odor of the substituted paraffin hydrocarbons, and upon analysis it gave a percentage of bromine corresponding to that required for monobrom-heptylene:

0.1850 gram of the substance gave 0.1116 gram AgBr.

	Calculated for $C_7H_{15}Br$ .	Found.
Br	46.93	46.57

With bromine this product united with a violent reaction, and the resulting oil gave the percentage of bromine required for dibrom-heptylene:

0.1938 gram of the substance gave 0.2797 gram AgBr.

	Calculated for $C_7H_{14}Br_2$ .	Found.
Br	62.01	61.42

This fraction therefore consists principally of a heptylene probably identical with that obtained by Pelletier and Walthier from the coal-oil of Amiano.<sup>1</sup>

Upon the addition of alcoholic mercuric chloride to fraction 110°–125° (atmospheric pressure), a fine, crystalline precipitate was formed that contained the percentage of mercury required for methyl sulphide:

0.3156 gram of the mercury compound gave 0.2214 gram HgS.

	Calculated for $(\text{CH}_3)_2\text{S} \cdot \text{HgCl}_2$ .	Found.
Hg	60.06	60.47

The fraction 125°–135° also gave a crystalline precipitate with alcoholic mercuric chloride, which after crystallisation from benzene gave a percentage of mercury corresponding to ethyl sulphide:

0.5056 gram of the mercury compound gave 0.3122 gram HgS.

	Required for $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{HgCl}_2$ .	Found.
Hg	55.40	55.42

Although the boiling-points of the oils from which these mercury addition-products were separated, were considerably higher than those of the sulphides to which the mercury-determinations correspond, these oils consisted to a certain extent of hydrocarbons which were subsequently found to contain no sulphur. The higher fractions gave, with mercuric chloride, oily addition-products which became crystalline after washing with alcohol, and separation from hot benzene. The addition-product from fraction 150°–155° gave 53.33 per cent. Hg; calculated for  $(\text{C}_3\text{H}_7)_2\text{SHgCl}_2$ , 51.41 per cent. Hg. It was therefore probably a mixture of propyl and butyl sulphides. From fraction 155°–160° the addition-product with mercuric chloride gave upon analysis 49.44 per cent. Hg; required for  $(\text{C}_4\text{H}_9)_2\text{SHgCl}_2$ , 47.96 per cent. Hg. It therefore still contained a lower sulphide. On account of the small quantity of these products obtained, we were unable to separate them more completely.

We will next describe in detail the separation of the various sulphides.—

#### *Methyl Sulphide.*

Further attempts were made to separate the lower sulphides from the crude naphtha distillate. We procured from Findley oil 250 liters of crude naphtha that nearly all distilled below 150°,

<sup>1</sup> Berzelius' Jsb. 21, 470.



and agitated it thoroughly in quantities of five liters each, with aqueous mercuric chloride. The heavy, flocculent precipitate that separated was subjected to heavy pressure in a screw press, dried, and decomposed by hydric sulphide in presence of alcohol. For the decomposition of considerable quantities of the mercury addition-product, vigorous agitation was necessary, and the mercuric sulphide invariably separated in the form of the red modification. After filtration, the alcoholic solution of the oil was diluted with water, the oil collected in a separatory funnel, washed, dried, and submitted to fractional distillation. It was nearly colorless, with a specific gravity of 0.8543 at 20°. Distilled under atmospheric pressure the decomposition was less marked than in the case of the oil extracted with sulphuric acid. A small quantity of the oil was collected below 50° that gave a percentage of sulphur corresponding to methyl sulphide—

0.1800 gram of the oil gave by the method of Carius 0.6672 gram BaSO<sub>4</sub>.

	Calculated for (CH <sub>3</sub> ) <sub>2</sub> S.	Found.
S	51.61	50.89

Between 60° and 80° the quantity of distillate was too small to prove the presence of methyl-ethyl sulphide. Results of analysis were intermediate between the requirements for methyl and ethyl sulphides, but not sufficiently close for methyl-ethyl sulphide. On account of the great amount of labor involved in the separation of these volatile oils, no further attempts were made to identify this sulphide, especially as its presence was regarded as doubtful.

#### *Ethyl Sulphide.*

After long-continued fractional distillations, we succeeded in obtaining a product distilling between 88° and 92° that gave a percentage of sulphur corresponding to ethyl sulphide—

0.1632 gram of the oil gave 0.4183 gram BaSO<sub>4</sub>.

	Calculated for (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S.	Found.
S	35.55	34.86

#### *Ethyl-propyl Sulphide.*

At several points between 91° and 130°, the boiling-points respectively of ethyl and propyl sulphides, distillates collected in considerable quantities. A fraction that distilled at 110°–112°

contained the percentage of sulphur required for ethyl-propyl sulphide—

0.2445 gram of the substance gave 0.5396 gram  $\text{BaSO}_4$ .

	Calculated for $\left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_3\text{H}_7 \end{smallmatrix} \right\} \text{S}$ .	Found.
S	30.77	30.31

The platinum salt was formed by the addition of alcoholic chlor-platinic acid, and it gave on analysis the required percentage of platinum—

0.3240 gram of the substance gave 0.1158 gram Pt.

	Calculated for $[(\text{C}_2\text{H}_5, \text{C}_3\text{H}_7)\text{S}]_2, \text{PtCl}_4$ .	Found.
Pt	36.01	35.75

The quantity of this sulphide obtained was insufficient for complete examination, and further study of it, as well as of other fractions of low boiling-points, must therefore be postponed until we can secure a larger supply of material.

#### *Normal Propyl Sulphide.*

All attempts to isolate iso-propyl sulphide were unsuccessful; very little of the distillate collected between  $115^\circ$  and  $125^\circ$ , and analysis showed that it could not be the iso-propyl compound that boils at  $120^\circ$ . The fraction  $115^\circ$ – $120^\circ$  gave 29.29 per cent. S, and the fraction  $120^\circ$ – $125^\circ$ , 28.52 per cent. S; calculated for  $(\text{C}_3\text{H}_7)_2\text{S}$ , 27.12 per cent. S. Analysis of platinum salts of these fractions gave similar results. Normal propyl sulphide was readily identified in the fraction  $127^\circ$ – $132^\circ$ , which collected in larger quantities—

0.0443 gram of the substance gave 0.0880 gram  $\text{BaSO}_4$ .

	Calculated for $(\text{C}_3\text{H}_7)_2\text{S}$ .	Found.
S	27.12	27.44

The presence of propyl sulphide was further shown by analysis of the platinum salt—

I. 0.1720 gram of the salt gave 0.0600 gram Pt.

II. 0.1309 gram of the salt gave 0.0457 gram Pt.

III. 0.0930 gram of the salt gave 0.0329 gram Pt.

	Calculated for $[(\text{C}_3\text{H}_7)_2\text{S}]_2, \text{PtCl}_4$ .	I.	Found. II.	III.
Pt	34.26	34.10.	34.92	35.15

Analyses II and III were made of preparations from fraction  $80^\circ$ – $90^\circ$  ( $P = 150$  mm.) that were obtained in fractioning the oil

from the sulphuric-acid extract. This oil contained only very small quantities of propyl sulphide, or of its lower homologues. It consisted mainly of higher sulphides and of sulphur-free oils. The presence of heptylene has been described, and nearly all fractions contained sulphur-free oils that united readily with bromine, and those of lower boiling-points with hydrobromic acid. The sulphides were separated by dissolving the oil in alcohol, and adding a small excess of alcoholic mercuric chloride. An aqueous solution precipitates the sulphides, but it is apt to carry down the sulphur-free oil. The precipitates were usually in the form of a thick, viscous mass, although with care they could be obtained crystalline. They were washed with alcohol, and decomposed with hydric sulphide in presence of alcohol. The filtered alcoholic solution was diluted with water, and the sulphide that separated was washed free from hydric sulphide, dried, and again submitted to fractional distillation for analysis.

Upon dilution of the alcohol from the precipitation by mercuric chloride, an oil separates that is lighter than water, and possesses an exceedingly disagreeable odor. These oils unite readily with bromine and with hydrobromic acid, and they contain no sulphur. Whether they are decomposition-products resulting from the action of sulphuric acid upon the sulphur-oils, or are normal constituents of the crude petroleum, we have not fully determined. But since the sludge-acid showed very little indication of decomposition, it seems probable that the sulphur-free oils are abstracted by sulphuric acid during the process of refining.

The composition of the fractioned sulphides before and after treatment with mercuric chloride may be shown by the effect on the percentage of sulphur. The fraction  $135^{\circ}$ – $140^{\circ}$  ( $P = 150$  mm.; B. P. =  $185^{\circ}$ – $190^{\circ}$ ,  $P$  normal) gave 15.40 per cent. S. After treatment with mercuric chloride as described above, analysis showed 20.37 per cent. S.

The higher sulphides were all obtained from fractions of the oil that was extracted from sludge-acid. Those of medium boiling-points may be separated in smaller quantities from naphtha-distillates by mercuric chloride, which has the advantage that the sulphides are uncontaminated by other products. But this method is exceedingly laborious, and the yields are small. We have in mind a modification that works successfully with small quantities of the mercury addition-product. It includes recovery of the mercury by conversion of the sulphide into the sulfoxide.

*Ethyl-pentyl Sulphide.*

After the twenty-second distillation (page 235) from fraction  $95^{\circ}$ – $100^{\circ}$  ( $P = 100$  mm.), a sulphide was obtained, through the mercury compound, that distilled without decomposition at  $156^{\circ}$ – $160^{\circ}$ . It gave, upon analysis, the percentage of sulphur required for ethyl-pentyl sulphide (B. P.  $158^{\circ}$ – $159^{\circ}$ ).

I. 0.2629 gram of the oil gave 0.4516 gram  $\text{BaSO}_4$ .

II. 0.1169 gram of the oil gave 0.2056 gram  $\text{BaSO}_4$ .

S	Calculated for $\left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_6\text{H}_{11} \end{smallmatrix} \right\} \text{S.}$	I.	Found.	II.
	24.24	23.59		24.15

*Iso-butyl Sulphide.*

The mercury addition-product from fraction  $110^{\circ}$ – $115^{\circ}$  ( $P = 100$  mm.) was decomposed with hydric sulphide, and the alcoholic solution diluted with water. After drying over calcic chloride, the oil, thus obtained, distilled at  $170^{\circ}$ – $176^{\circ}$ , which corresponded to the boiling-point of iso-butyl sulphide ( $172^{\circ}$ ), and its composition was further shown by a determination of sulphur—

0.1750 gram of the oil gave 0.2760 gram  $\text{BaSO}_4$ .

S	Calculated for $(\text{C}_4\text{H}_9)_2\text{S.}$	Found.
	21.92	21.66

*Normal Butyl Sulphide.*

The fraction  $117^{\circ}$ – $125^{\circ}$  ( $P = 100$  mm.) gave an addition-product with mercuric chloride from which an oil was obtained that distilled at  $180^{\circ}$ – $185^{\circ}$  (B. P. of normal butyl sulphide  $= 182^{\circ}$ ), and the percentage of sulphur indicated butyl sulphide—

I. 0.1633 gram of the oil gave 0.2657 gram  $\text{BaSO}_4$ .

II. 0.2929 gram of the oil gave 0.3236 gram  $\text{BaSO}_4$ .

S	Calculated for $(\text{C}_4\text{H}_9)_2\text{S.}$	I.	Found.	II.
	21.92	22.35		21.07

*Butyl-pentyl Sulphide.*

An inspection of the weights of distillate collected at different temperatures given on page 235 will show a tendency of the distillates to collect at certain temperatures, and this is especially evident in the fraction  $135^{\circ}$ – $140^{\circ}$ . As the distillation proceeded, the fractions at these points increased in quantity, and, so far as

examined, each of them corresponded to a definite sulphide. From the fraction  $135^{\circ}$ – $140^{\circ}$ , by decomposition of the addition-product with mercuric chloride, an oil was obtained that distilled at  $185^{\circ}$ – $190^{\circ}$  (Bar. = 740 mm.), and the percentage of sulphur corresponded to butyl-pentyl sulphide—

I. 0.2509 gram of the oil gave 0.3721 gram  $\text{BaSO}_4$ .

II. 0.2676 gram of the oil gave 0.3925 gram  $\text{BaSO}_4$ .

S	Calculated for $\left\{ \begin{smallmatrix} \text{C}_4\text{H}_9 \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right\} \text{S}$ .	Found.	
		I.	II.
	20.00	20.37	20.14

It is hardly probable that this product was a mixture of butyl and pentyl sulphides, since it was obtained at different times after prolonged distillation. It will be further examined.

#### *Pentyl Sulphide.*

This sulphide was separated from the fraction  $150^{\circ}$ – $155^{\circ}$  ( $P = 100$  mm.) by conversion into the mercury compound, and decomposition with hydric sulphide. Different preparations from independent fractions distilled, with very little decomposition, at  $205^{\circ}$ – $210^{\circ}$  (Bar. = 745.5 mm.), which is somewhat lower than the boiling-point assigned to pentyl sulphide ( $216^{\circ}$ ). But from the results of analysis there can be no doubt as to the composition of this sulphide—

I. 0.1987 gram of the oil gave 0.2717 gram  $\text{BaSO}_4$ .

II. 0.2723 gram of the oil gave 0.3716 gram  $\text{BaSO}_4$ .

III. 0.2844 gram of the oil gave 0.3902 gram  $\text{BaSO}_4$ .

S	Calculated for $(\text{C}_5\text{H}_{11})_2\text{S}$ .	Found.		
		I.	II.	III.
	18.39	18.75	18.74	18.85

It is quite probable that the low boiling-point was due to the presence of a very small quantity of a lower sulphide, since the sulphur-determinations are somewhat higher than the percentage required for pentyl sulphide.

#### *Hexyl Sulphide.*

From the fraction  $160^{\circ}$ – $170^{\circ}$  ( $P = 100$  mm.), by precipitation with mercuric chloride and decomposition with hydric sulphide, a light-yellow oil was obtained that distilled with some decomposition at  $225^{\circ}$ – $235^{\circ}$ , and gave the percentage of sulphur required for hexyl sulphide—

0.3110 gram of the oil gave 0.3531 gram  $\text{BaSO}_4$ .



	Calculated for $(C_6H_{13})_2S$ .	Found.
S	15.84	15.59

At least one-third of the original oil distilled above the boiling-point of hexyl sulphide, but with considerable decomposition, even under diminished pressure. It consisted to a very large extent of sulphides, but we have not attempted to separate them for identification.

In order to overcome any doubt that these sulphides are contained in the crude petroleum, we distilled several liters under diminished pressure (to avoid decomposition), and extracted portions of various distillates with sulphuric acid, and other portions with aqueous mercuric chloride. The oils, separated from the acid solution and from the mercuric chloride addition-product, resembled in all respects the products previously described. From the distillate corresponding to  $150^{\circ}$ – $300^{\circ}$  (atmospheric pressure), or to the best grades of burning-oil, by agitation with aqueous mercuric chloride, the characteristic heavy precipitate was formed, and the oil obtained from it contained 19.72 per cent. sulphur and gave all the reactions for sulphides. In separating sulphides from oils extracted with sulphuric acid, we have frequently obtained small quantities of a product with a penetrating odor resembling that of turpentine; and, at other times, oils containing no sulphur, but with an odor characteristic of certain ethereal oils, such as peppermint or pennyroyal. We have not yet obtained these oils in quantity sufficient for examination.

The study of Ohio oils will be continued, and the investigation will include an examination of oils from other localities, for sulphur compounds, and also of the composition of other acid-residues and by-products obtained in refining petroleum oils.

CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE.

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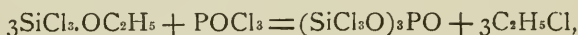
# ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON THE ETHERS AND CHLORHYDRINES OF SILICIC ACID.

BY H. N. STOKES.

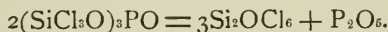
That silica can combine with other acids, forming mixed anhydrides, has long been known, and several such bodies have been described. Friedel and Ladenburg<sup>1</sup> obtained the tetra-acetyl derivative  $\text{Si}(\text{O}.\text{CO}.\text{CH}_3)_4$  by treating silicon tetrachloride with acetic acid or anhydride. Friedel and Crafts<sup>2</sup> obtained  $\text{Si}(\text{OC}_2\text{H}_5)_3\text{O}.\text{CO}.\text{CH}_3$  from ethyl orthosilicate and acetic anhydride. Hautefeuille and Margottet<sup>3</sup> described a crystalline compound,  $\text{SiO}_2.\text{P}_2\text{O}_5$ , formed by fusing amorphous silica with metaphosphoric acid.

By the action of phosphorus oxychloride on silicic ethers and their chlorine derivatives, I have obtained bodies which consist of phosphoryl chlorides in which the chlorine is partly replaced by a residue of silicic acid, and which are therefore chlorides of silicophosphoric acids.

Phosphorus oxychloride was caused to react upon *orthosilicic ethyl-trichlorhydrine*,  $\text{SiCl}_3.\text{OC}_2\text{H}_5$ , hoping thereby to obtain the silicon oxychloride described by Friedel and Ladenburg<sup>4</sup> and by Troost and Hautefeuille<sup>5</sup>:



and



The experiment proved that this reaction does not take place.

If the trichlorhydrine be heated in a sealed tube with an excess of phosphorus oxychloride, no reaction is apparent below  $175^\circ$ , the contents remaining perfectly clear. If the temperature be kept at  $180^\circ$ – $200^\circ$ , a white, amorphous substance is soon formed which is sufficiently porous to absorb all the liquid products. After 2–3 hours' heating the tube is opened, when ethyl chloride escapes in large quantities. On placing the tube in an air-bath heated at about  $150^\circ$ , and connecting it with a condenser, a large amount of liquid may be collected. The solid remaining in the

<sup>1</sup> Ann. Chem. (Liebig) **146**, 174.

<sup>2</sup> Ann. chim. phys. [4] **9**, 47.

<sup>3</sup> Compt. rend. **96**, 1052.

<sup>4</sup> Ann. Chem. (Liebig) **147**, 355.

<sup>5</sup> Ann. chim. phys. [5] **7**, 465.

tube may then be freed from excess of phosphorus oxychloride by passing a current of dry air over it by means of a capillary.

The liquid, on fractioning, is readily separated into phosphorus oxychloride (boiling at  $110^{\circ}$ ) and silicon tetrachloride (boiling at  $57^{\circ}$ – $61^{\circ}$ ), though much of the latter is lost, being carried off by the ethyl chloride which is abundantly held in solution. The product obtained after six distillations was analysed.

	Calculated for $\text{SiCl}_4$ .	Found.
Si	16.52	16.24

The view with regard to its nature was confirmed by converting it into ethyl orthosilicate (boiling at  $165.5^{\circ}$ ). As the liquid passed over entirely below  $112^{\circ}$ , no silicon oxychloride was formed, and no substances other than those mentioned could be detected.

Analyses of the solid substance gave :

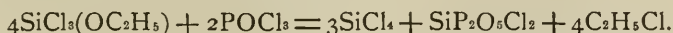
	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$ .	Found.	
		I.	II.
Si	10.92	10.17	10.06
P	24.15	25.16	25.11
Cl	27.59	27.33	...

The agreement is only approximate, as the substance could not be purified in any way; and on heating too long or at too high a temperature, when drying, phosphorus oxychloride is slowly given off. It is possibly a mixture of substances, in the formation of which the one supposed represents one stage. If heated above  $200^{\circ}$  phosphorus oxychloride is given off, and, at a red heat, phosphorus pentoxide; and the residue left at a white heat consists of amorphous silica imbedded in a vitreous substance, probably the compound  $\text{SiO}_2 \cdot \text{P}_2\text{O}_5$  of Hautefeuille and Margottet. The loss on heating corresponds to the equation—



	Calculated.	Found.
Loss,	49.01	51.86

The formation of the substance, which, for reasons given below, may be designated as *silico-pyrophosphoryl chloride*, is most simply expressed by the equation—



*Silico-pyrophosphoryl chloride* is a very bulky substance, resembling the lightest form of amorphous silica. It may be

obtained perfectly colorless, but is usually more or less colored by organic matter, formed by secondary reactions, when heated too high. It is extremely hygroscopic, and gives off hydrochloric acid instantly when exposed to moist air. It is readily soluble in absolute alcohol—a proof that it contains no free silica. The alcoholic solution, which probably contains an ether of silico-phosphoric acid, may be evaporated nearly to dryness, or heated any length of time at  $150^{\circ}$  without decomposition. On heating at  $225^{\circ}$  it soon deposits transparent, gelatinous silica. The solution in alcohol is attended with considerable rise of temperature. The substance is insoluble in ether. If cold water be poured on the fine powder it readily dissolves, with the exception of a few flakes of silica; but if first moistened, or if in lumps, most of the silica remains undissolved: the best way to get a clear aqueous solution is to dissolve in a little alcohol and then to dilute with water. The reaction with water alone is somewhat violent. The aqueous solution may be kept a long time—indeed, may be strongly concentrated on the water-bath—but on evaporation *to dryness* a vitreous mass is left, from which water extracts phosphoric acid only.

All attempts to prepare salts of silico-phosphoric acid have failed. Ammonium carbonate precipitates gelatinous silica. If the cold aqueous solution, prepared as described above, be acidified with nitric acid, excess of silver nitrate added, and filtered from silver chloride, a clear solution is obtained. If to this be added, drop by drop, dilute ammonia, a white precipitate is formed, which at a certain point changes to yellow. The analysis of the white substance (dried at  $100^{\circ}$ ) gave—

	Calculated for $\text{Ag}_4\text{P}_2\text{O}_7$	Found.
Ag	71.17	71.25

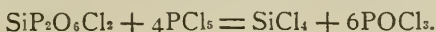
The yellow precipitate proved to be merely silver ortho-phosphate.<sup>1</sup> The filtrate from the silver salts gives an abundant pre-

<sup>1</sup> The reaction described above affords a convenient method for separating, at least approximately, ortho- from pyro-phosphoric acid. A solution of the acids—or their soluble salts—is acidified in the cold with nitric acid, and silver nitrate added in excess. On adding dilute ammonia, drop by drop, all the pyro-phosphoric acid is precipitated before any of the ortho-phosphoric acid comes down. At this point a single drop of ammonia gives a yellow tinge to the precipitate, which a drop of dilute nitric acid causes to disappear. If the liquid be now filtered, all the pyro-phosphoric acid will be in the precipitate and all the ortho-phosphoric acid in the filtrate. The reaction is so sharp that it might possibly be used to separate the acids quantitatively.

precipitate of silicic acid, when warmed with ammonia. The magnesia precipitate also shows the characteristic reaction of magnesium pyro-phosphate, dissolving in acetic acid when precipitated in the cold, and being reprecipitated from this solution on boiling.

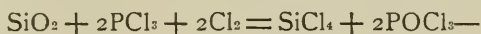
The substance is therefore a derivative of pyro-phosphoric acid, and the formation of some ortho-phosphoric acid may be explained by the decomposition of the former—pyro-phosphoryl chloride dissolving in water with formation of ortho-phosphoric acid.<sup>1</sup>

Heated with phosphorus pentachloride at 100°, silico-pyro-phosphoryl chloride is readily and quantitatively converted into silicon tetrachloride and phosphorus oxychloride:

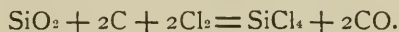


The tetrachloride was isolated and expectations with regard to its nature were confirmed on converting it into the ether (b. p., 165.5°). No silicon oxychloride could be obtained. If heated with an insufficient amount of phosphorus pentachloride, the excess remains apparently unchanged.

The conversion of a derivative of silicic acid into silicon tetrachloride at so low a temperature has not been hitherto observed. R. Weber<sup>2</sup> obtained the tetrachloride and phosphorus oxychloride by passing the vapor of phosphorus pentachloride over silica at a red heat. As the pentachloride is completely dissociated at 300° into trichloride and chlorine, the reaction is due to the action of chlorine, combined with the reducing action of the trichloride—



which is analogous to the old method of preparing the tetrachloride—



As I have convinced myself, phosphorus pentachloride does not act on amorphous silica (dried at 100°) even at 250°, further than to dehydrate it.

The action of a smaller quantity of phosphorus oxychloride on the trichlorhydrine is similar. 3 mol. trichlorhydrine and 1 mol. oxychloride, heated at 180°, gave ethyl chloride, silicon tetrachloride, and a solid product completely soluble in alcohol and water, the composition of which differed, however, from that of the substance above described. (Found: Si, 15.25; P, 22.30; Cl, 14.13.)

<sup>1</sup> Michaelis: Ber. d. chem. Ges. 4, 767.

<sup>2</sup> Ann. der Phys. Pogg. 112, 619.



The action of an excess of phosphorus oxychloride on the chlorhydrines  $\text{SiCl}_2(\text{OC}_2\text{H}_5)_2$  and  $\text{SiCl}(\text{OC}_2\text{H}_5)_3$  is essentially similar. At  $180^\circ$ – $200^\circ$  a solid substance is formed, with much ethyl chloride and silicon tetrachloride. The amount of the tetrachloride is directly, and that of the solid inversely proportional to the amount of chlorine in the chlorhydrine. In each case the tetrachloride was isolated in a state of approximate purity, and converted into the ortho-ether, boiling at  $165.5^\circ$ . No other volatile substances could be detected. The solid body was completely soluble in alcohol, and, in brief, showed all the properties above described as belonging to silico-pyro-phosphoryl chloride.

The analysis of the product from  $\text{SiCl}_2(\text{OC}_2\text{H}_5)_2$  gave—

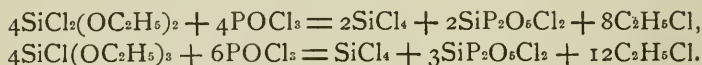
	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$ .	Found.	
		I.	II.
Si	10.92	11.68	11.80
P	24.15	24.53	24.91

The product from  $\text{SiCl}(\text{OC}_2\text{H}_5)_3$  gave—

	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$ .	Found.
Si	10.92	10.15
P	24.15	24.54
Cl	27.59	24.73

The results, as before, are only approximate; but, it must be remembered, the body loses phosphorus oxychloride slowly on heating, and only the crude product could be analysed.

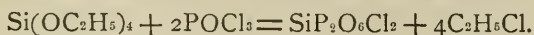
The reactions in these cases are—



*Orthosilicic ether*,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , was heated with excess of phosphorus oxychloride for two hours at  $180^\circ$ – $200^\circ$ . The tubes contained a solid substance and ethyl chloride. On distilling off the excess of oxychloride and decomposing it with water, only a trace of silica was left after evaporation, showing that practically no volatile silicon compound was formed. The solid, the properties of which were in every respect identical with those of the body above described, gave on analysis—

	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$ .	I.	Found.	
			II.	III.
Si	10.92	9.92	10.05	10.21
P	24.15	25.52	25.63	25.84
Cl	27.59	29.66	29.90	...

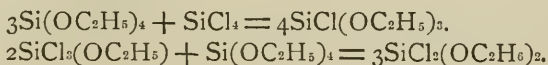
The reaction is, therefore, represented by the equation—



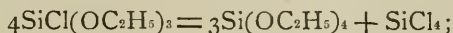
The constitution of the silico-phosphoryl chloride is possibly very complex. The simplest constitutional formula, deduced from

the last equation, would be  $\text{Si} \begin{Bmatrix} \text{O} > \text{POCl} \\ \text{O} > \text{POCl} \end{Bmatrix}$ ; but as this would

give no pyro-phosphoric acid on decomposition with water, we must assume that it is  $\text{SiO} < \begin{smallmatrix} \text{O}.\text{PO}.\text{Cl} \\ \text{O}.\text{PO}.\text{Cl} \end{smallmatrix} > \text{O}$ ; or a polymer containing the group  $-\text{O}.\text{PO}.\text{O}.\text{PO}.\text{O}-$ , which makes it a derivative of metasilicic acid. The cause of the formation of silicon tetrachloride from the chlorhydrines is not clear. It is obviously not due to a direct replacement of ethoxyl by chlorine, for then it should be obtained in the same amount from each chlorhydrine, or from the ether; whereas the latter does not give it, and the amount obtained from the former is proportional to the amount of chlorine they already contain. Besides, no phosphoric ethers are formed. Nor does the supposition explain the formation of silico-pyrophosphoryl chloride in quantities inversely as the amount of chlorine. A possible explanation is the following: The chlorhydrines<sup>1</sup> are formed by heating mixtures of ortho-silicic ether with silicon tetrachloride, or of either of these with other chlorhydrines, that one being formed in largest amount which corresponds in composition to the mean composition of the mixture; for example—



These reactions take place below  $200^\circ$ : partial dissociation occurring, the products reuniting to form that body which tends to give the liquid a homogeneous composition. Doubtless the reverse process takes place at the same time; for example—



and if phosphorus oxychloride be present—which, as just shown, destroys the ether—this can go on until all the chlorhydrine has been converted into ether and tetrachloride. This explanation is

<sup>1</sup> Friedel and Crafts: *Ann. chim. phys.* [4] 9, 11, 14, 15.

simple enough, but, as shown by the action of phosphorus oxychloride on *disilicic* chlorhydrines, the actual process is possibly more complicated.

By heating a mixture of trichlorhydrine, phosphorus and iodine, a solid of similar properties was obtained, and silicon tetrachloride was formed. The reaction was not followed further.

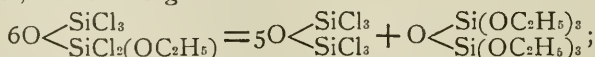
*Action of Phosphorus Oxychloride on Derivatives of Disilicic Acid.*

*Hexethyl disilicate*,<sup>1</sup>  $\text{O} \begin{smallmatrix} \text{Si}(\text{OC}_2\text{H}_5)_3 \\ \text{Si}(\text{OC}_2\text{H}_5)_3 \end{smallmatrix}$ , was heated with an excess of phosphorus oxychloride in sealed tubes at 180°–200° for two or three hours. The tubes contained a white solid, outwardly resembling silico-pyrophosphoryl chloride, and much ethyl chloride. No volatile silicon compound was formed. The solid resembled in its general properties the one described. It was completely soluble in alcohol, and therefore contained no free silica. The solution gave the reactions of pyro-phosphoric acid. It differed markedly in composition from the *ortho-silicic* derivative, the analysis giving—

	Calculated for $\text{SiP}_2\text{O}_6\text{Cl}_2$ .	Found.
Si	10.92	17.03
P	24.15	23.91
Cl	27.59	21.04

This corresponds to no probable formula, but contains 4 atoms Si to 5 atoms P, instead of 1 atom Si to 2 atoms P. Phosphorus pentachloride converts it readily (at 100°) into silicon tetrachloride and phosphorus oxychloride. No silicon oxychloride is formed, the product passing over entirely below 112°. The tetrachloride was isolated and converted into the tetrethyl ether (boiling at 165.5°).

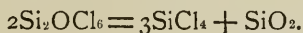
The ease with which the *ortho-chlorhydrines* give, with phosphorus oxychloride, silicon tetrachloride, led to an analogous experiment with the *disilicic chlorhydrines*, in the hope that in this way silicon oxychloride might be obtained. On the above hypothesis, we should have, in the presence of phosphorus oxychloride, the following reaction :



and analogous reactions with the other chlorhydrines.

<sup>1</sup> Friedel and Crafts : *Ann. chim. phys.* [4] 9, 24.

The disilicic chlorhydrines, which have not hitherto been prepared, are formed by heating disilicic ether with an excess of silicon tetrachloride for several hours at 200°. A gradual exchange of ethoxyl and chlorine occurs, disilicic chlorhydrines and ortho-silicic trichlorhydrine being formed. After distilling off the latter, the residue is again heated with silicon tetrachloride, whereby the conversion is carried further. In this way a mixture of disilicic chlorhydrines was obtained, which, after freeing from all ortho-silicic compounds by repeated distillation, boiled at 170°–220°. A chlorine determination showed that it contained the equivalent of 65 per cent.  $\text{Si}_2\text{OCl}_6$ . No attempt was made to isolate any of these chlorhydrines, as no less than eight are theoretically possible, and it was presumed that they would all act in the same way toward phosphorus oxychloride. The mixture was heated with excess of phosphorus oxychloride (based on the amount of chlorine shown by analysis) for two and a half hours at 180°–200°; after which no further action was observed. The appearance of the product was the same as in previous experiments. The liquid product was distilled off and fractioned. It was found to consist of an excess of phosphorus oxychloride, of *silicon tetrachloride*, which was recognised through conversion into the ether, and ethylchloride. The liquid boiled entirely below 112°, and therefore none of the expected silicon oxychloride was formed. The solid product was markedly different from those before obtained. It was only partly soluble in alcohol, and on boiling out with the solvent, a large residue of *silica* was left. Besides a soluble silico-phosphoryl chloride and ethyl chloride, the only products were silicon tetrachloride and silica. If the oxychloride be formed at all, it is at once decomposed in the presence of phosphorus oxychloride—



Whether this actually occurs is questionable, as the oxychloride and all the other substances concerned are, by themselves, stable at a much higher temperature than that employed. I am unable to give any satisfactory explanation of the reaction.

Amorphous silica, prepared from water-glass and dried at 100°, gives with phosphorus oxychloride a small amount of silico-phosphoryl chloride, soluble in alcohol: 3.5 per cent. of the silica was converted into this compound.

The silicon tetrachloride used as the starting-material of these experiments was made by the admirable method of Gattermann.<sup>1</sup> For preparing the silicon mixture I used, instead of test-tubes, sheet-iron crucibles of about 200 cc. capacity. These are nearly filled with an intimate mixture of three parts quartz powder and one part magnesium powder, tightly pressed down. On heating over a blast-lamp, the reaction starts in a few seconds, and is indicated by the whole crucible suddenly becoming red-hot. During the reaction the lid must be held down firmly. I prefer to extract the magnesia from this product before using it, as less care has to be used in regard to temperature when passing chlorine over it. By using ice alone, to condense the chloride, nearly the theoretical yield is obtained: the crude product loses about 15 per cent. in the process of purification.

The *orthochlorhydrines* were prepared essentially according to the method of Friedel and Crafts (*l. c.*). Any mixture may be used which coincides in composition with that of the chlorhydrine desired. The yield is never theoretical, no matter how long the heating may be continued. The yields of pure substance, obtained after six distillations, were as follows: Monochlorhydrine, 65 per cent.; dichlorhydrine, 40 per cent.; trichlorhydrine, 47 per cent. More can, of course, be obtained by uniting and heating the residues.

Friedel and Crafts<sup>2</sup> obtained the disilicic ether by adding to silicon tetrachloride, drop by drop, alcohol containing the calculated amount of water. They claim that the yield is nearly theoretical. I am not able to confirm this statement. By following their directions exactly, I obtained a mixture of ortho and disilicic ethers, with ethers of much higher boiling-points. After repeated fractioning, only 33 per cent. of the theoretical yield of disilicic ether was obtained, and the amount of ortho-ether was much greater. This is due to the fact that the added water acts on the disilicic ether already formed, giving more complex bodies, so that there is an excess of tetrachloride, which is converted into ortho-ether.

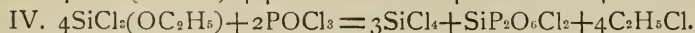
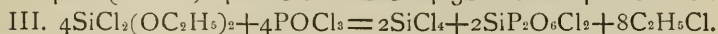
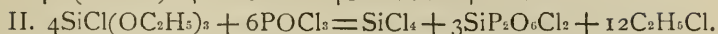
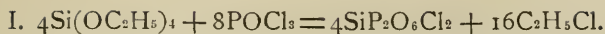
The essential results of these experiments may be summed up as follows:

Phosphorus oxychloride acts on orthosilicic ether and its chlorine derivatives according to the following equations:

<sup>1</sup> Ber. d. chem. Ges. **22**, 186-8.

<sup>2</sup> Ann. chim. phys. [4] **9**, 26.





The body  $\text{SiP}_2\text{O}_6\text{Cl}_2$  is the chloride of a silico-pyrophosphoric acid, is decomposed by water into silica and pyrophosphoric acid, and is easily converted by phosphorus pentachloride into silicon tetrachloride and phosphorus oxychloride.

The ether of disilicic acid acts similarly, giving a silico-phosphoryl chloride of different composition but analogous properties.

The chlorhydrines of disilicic acid do not give with phosphorus oxychloride, as might be inferred, a silico-phosphoryl chloride and silicon oxychloride, but a mixture of the first with free silica and silicon tetrachloride.

Phosphorus trichloride also acts on orthosilicic ether at  $200^\circ$ , giving a white solid, and liquid products, which will be further studied.

In conclusion, I wish to express my indebtedness to Prof. F. W. Clarke for liberally placing at my disposal the means of carrying out these experiments.

U. S. GEOLOGICAL SURVEY, WASHINGTON, *February*, 1891.

## ON THE ATOMIC WEIGHT OF OXYGEN.

BY E. H. KEISER.

In a recent paper<sup>1</sup> on this subject, Mr. W. A. Noyes makes a statement which is not in accordance with the facts, and which, as it may be misleading to some, deserves to be corrected. Mr. Noyes states that he has pointed out a source of error in my determinations of the atomic weight of oxygen. I desire to call attention to the fact that Mr. Noyes has merely pointed out what he *supposes* to be a source of error in my determinations, which is quite different from having pointed out a source of error. Moreover, Mr. Noyes's supposition is not well founded, and is not in accordance with the results of experiments.

<sup>1</sup> Journal of Analytical and Applied Chemistry 5, 36; Ber. d. chem. Ges. 24, 238.

The point in question is this: It was found as the result of direct experiments that the hydrogen which was driven out of the palladium tube contained a trace of moisture; this moisture was collected in a phosphorus-pentoxide tube, and its weight was subtracted from the apparent weight of hydrogen. Mr. Noyes thinks that there could not have been moisture present in the hydrogen, and that the increase in weight of the pentoxide tube should not have been deducted from the apparent weight of hydrogen. But I had found by direct experiment that moisture was present, and was, therefore, obliged to insert a weighed phosphorus-pentoxide tube. Mr. Noyes thinks that the moisture came from the gases that were subsequently passed through the tube, but, as I have clearly stated in my paper, these gases were thoroughly dried by passing through concentrated sulphuric acid and over phosphorus pentoxide before entering the tube in question, so that this supposition is also without foundation.

The fact remains that the atomic weight of oxygen as determined by the combustion of weighed amounts of hydrogen, the hydrogen being obtained from palladium hydrogen, is 15.95, and not a lower value, as Mr. Noyes thinks he has shown it to be. Nor can I agree with his statement that it is almost certain that the true atomic weight of oxygen is not greater than 15.90. Before coming to such a conclusion, it is well to remember that all recent determinations of this atomic weight, like the older ones of Dumas, and Erdmann and Marchand, have been determinations of the composition of water *by difference*, that is, only two of the three quantities have been determined directly. In all the determinations it is assumed that the hydrogen or oxygen which is weighed is really all present in the weighed quantity of water, or, that the hydrogen and oxygen which have been weighed have combined completely with one another. In other words, no *complete syntheses* of water have yet been recorded. - The words *complete syntheses* are here used in the sense in which they were used by Stas in his researches on the atomic weights of silver, chlorine, etc. To make a complete synthesis of water it is necessary to weigh separately the hydrogen, the oxygen, and the water formed by the union of the weighed amounts of hydrogen and oxygen. It seems to me that it is too early to come to any conclusion as to the true value of the relation between hydrogen and oxygen until this relation shall have been determined by the complete gravimetric synthesis of water.

I have recently made determinations of the atomic weight of oxygen by a method which permits of the separate weighing of the hydrogen, the oxygen and the water. In brief the method is as follows: A glass vessel containing spongy palladium and provided with a three-way stop-cock is exhausted with an air-pump, and as perfect a vacuum obtained as is possible with a mercury-pump, and the weight of the empty vessel determined. Pure hydrogen from hot palladium is passed over phosphorus pentoxide and into the exhausted vessel. After the spongy palladium is saturated with the gas, the vessel is again exhausted, and the increase in weight after again weighing is the weight of hydrogen occluded. Pure oxygen is now admitted to the palladium hydrogen until present in excess; the hydrogen is completely converted into water at low temperatures. The weight of oxygen admitted is determined by again weighing the vessel. Now a weighed phosphorus-pentoxide U-tube is attached to the palladium vessel, and the excess of oxygen, together with any nitrogen if it was present in the oxygen, is removed by the air-pump. The loss in weight of the palladium vessel and the pentoxide tube (both weighed together) gives the excess of oxygen. The water is thereupon completely transferred from the palladium to the pentoxide tube, and the increase in weight of the latter gives the weight of water formed. The weights of the hydrogen, oxygen and water are thus determined separately and by direct weighings. Two weighings are involved in the determination of the hydrogen, two weighings also give the weight of water, and from three weighings the weight of oxygen is obtained. Thus far I have made three determinations, and in each one the sum of the weights of hydrogen and oxygen agrees with the weight of water found to within .2 of a milligram, and the weight of the palladium tube at the end of the determination was found to be the same as at the beginning. The three results agree quite closely with one another, and give for the atomic weight of oxygen almost exactly the whole number, 16. After a larger number of determinations have been made I shall publish the details of the method and of each separate determination.

I shall not here enter into a critical discussion of the method used by Mr. Noyes. It might lead to a controversy and a waste of time. It would, however, not be difficult for any thoughtful reader of his paper to see where inaccuracies might perhaps

have crept into the work, and several sources of error have already been shown by Mr. G. S. Johnson<sup>1</sup> to exist in the method, which, it seems to me, have not been completely disproved by Mr. Noyes. Nor is it possible to regard the use of sticks of caustic potash for the purification of hydrogen as unobjectionable. The sticks, as Mr. Noyes states, gradually dissolved in the water carried over. But sticks of potash contain air, and when they dissolve the air is set free, and thus the hydrogen is rendered impure.

BRYN MAWR, PA., *March*, 1891.

## ON ORTHO-SULPHO-PARA-TOLUIC ACID AND SOME OF ITS DERIVATIVES.

BY WYATT W. RANDALL.

### *Introduction.*

Investigations upon the sulphonic acids derived from para-toluic acid by the replacement of a hydrogen atom of the benzene nucleus by the sulphoxyl group, —SO<sub>2</sub>H, have up to this time been almost entirely confined to that one of the two isomeric sub-

stances represented by the formula  $C_6H_3 \begin{cases} CO.OH & (1) \\ SO_2.OH & (3) \\ CH_3 & (4) \end{cases}$ ; that is,

meta-sulpho-para-toluic acid. Flesch,<sup>2</sup> Bechler,<sup>3</sup> Fischli,<sup>4</sup> Remsen and Burney,<sup>5</sup> R. Meyer and Baur,<sup>6</sup> and Remsen and Emerson<sup>7</sup> prepared this acid and examined its derivatives. On the other hand, the only work on record upon the isomeric acid,

$C_6H_3 \begin{cases} CO.OH & (1) \\ SO_2.OH & (2) \\ CH_3 & (4) \end{cases}$ , is that of Fittica,<sup>8</sup> who claims to have pre-

pared the substance from thio-thymol,  $C_6H_3 \begin{cases} CH_3 & (1) \\ SH & (3) \\ C_2H_7 & (4) \end{cases}$ , by oxida-

<sup>1</sup> Chem. News 59, 272.

<sup>2</sup> J. prakt. Chem. [2] 8, 167.

<sup>3</sup> This Journal 2, 405.

<sup>4</sup> This Journal 8, 264.

<sup>5</sup> Ber. d. chem. Ges. 6, 478.

<sup>6</sup> Ber. d. chem. Ges. 12, 616.

<sup>7</sup> Ann. Chem. (Liebig) 220, 18.

<sup>8</sup> Ann. Chem. (Liebig) 172, 327.

tion by means of nitric acid, and this thio-thymol in turn was obtained by the action of phosphorus pentasulphide upon thymol,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CH}_3 \\ \text{OH} \\ \text{C}_3\text{H}_7 \end{array} \right.$ . Fittica distinguishes between this ortho-sulpho-

para-toluic acid and its isomer by the following characteristics which he claims to have established, *viz.* (1) that the acid crystallises from a solution in alcohol without water of crystallisation, (2) that the acid is insoluble in water,<sup>1</sup> and (3) that it forms a magnesium salt which when crystallised from absolute alcohol contains no water of crystallisation. Further, he says that he was unable to prepare salts of the acid with potassium, sodium or barium, since with solutions of the hydroxides of these metals the crystallised acid blackened, and the solution after filtration contained the sulphur of the sulpho-acid in the form of sulphate. He gives 190° as the melting-point of the acid.

*"Methyl-saccharin."*

The investigations of Fittica upon ortho-sulpho-para-toluic acid and its derivatives were much hindered by reason of the difficulty of obtaining any of these compounds in pure form and in any quantity. Recently, however, a new sulphinide has been prepared which can be transformed with no great difficulty into ortho-sulpho-para-toluic acid, and which can be procured in sufficient quantity to render a thorough investigation of this field possible. This sulphinide is "methyl-saccharin," or, more properly,

para-toluic sulphinide, of the formula  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right. > \text{NH} \begin{array}{l} (1) \\ (2) \\ (4) \end{array}$ .

The method, use of which is made for its preparation, was devised by the "Badische Anilin- und Soda-fabrik,"<sup>2</sup> and is as follows: Para-toluidine is transformed into para-toluidine-meta-sulphonic acid<sup>3</sup>; by means of the Sandmeyer reaction<sup>4</sup> the amido group is replaced by cyanogen, forming para-cyan-toluene-meta-sulphonic acid. By the action of phosphorus pentachloride is formed the chloride of this acid, and from this the amide is prepared. This is then transformed into ortho-sulphonamine-para-toluic acid, and, finally, this acid, on being heated above its melting-point, passes

<sup>1</sup> See also Meyer and Baur, *Ann. Chem. (Liebig)* **220**, 22.

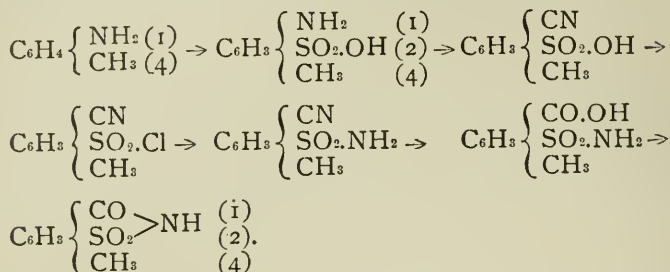
<sup>2</sup> *Ber. d. chem. Ges.* **22**, Referate, 719.

<sup>3</sup> Neville and Winther, *Ibid.* **13**, 1947.

<sup>4</sup> *Ibid.* **17**, 2650.



into para-toluic sulphinide. The successive products of these several reactions are represented by the following formulæ:

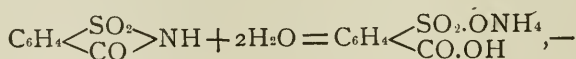


The Badische Anilin- und Sodafabrik most courteously placed at the disposal of Prof. Remsen the para-toluic sulphinide or "methyl-saccharin" which served as the starting-point in the present investigation, and at his suggestion I undertook the work, an account of which is given below.<sup>1</sup>

I may as well say at this point that in speaking of this substance as the "ortho-sulpho-," rather than the "meta-sulpho-," para-toluic acid, I have followed the nomenclature adopted by Beilstein in his "Handbuch der Organischen Chemie," and have prefixed such terms as will indicate the positions of the other groups with reference to the carboxyl group taken as the starting-point.

#### *Ortho-sulpho-para-toluic Acid.*

In order to obtain the free ortho-sulpho-para-toluic acid from para-toluic sulphinide, advantage was taken of the transformation brought about by boiling sulphinides with dilute hydrochloric acid. This reaction, studied by Remsen and Burton,<sup>2</sup> who experimented upon the transformation by its means of benzoic sulphinide into acid ammonium ortho-sulpho-benzoate,—



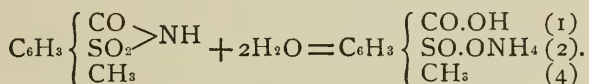
was equally applicable for the corresponding transformation of para-toluic sulphinide. The operation was conducted with portions of the sulphinide of 25 grams each, in flasks fitted with reflux-

<sup>1</sup>I take this opportunity of expressing my thanks to the Company for their liberality.—I. R.

<sup>2</sup>This Journal 11, 403-405.

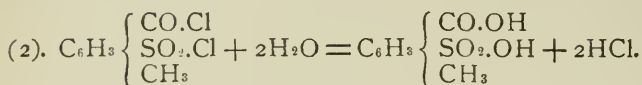
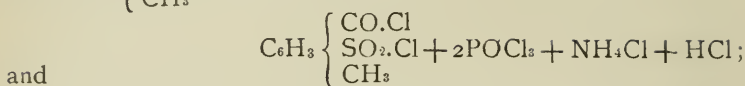
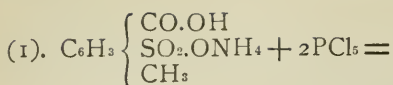
condensers. In each flask was poured 600 cc. dilute hydrochloric acid, prepared by mixing 100 cc. pure concentrated acid with 500 cc. water. After the boiling had been continued a half-hour, all the sulphinide had passed into solution. At the end of 45 or 50 minutes the heating was discontinued, and it was found that on cooling no sulphinide crystallised out. Moreover, the sweet taste had disappeared from the solution. The latter was then evaporated to dryness, to be rid of hydrochloric acid, redissolved and evaporated to crystallisation.

The transformation was precisely similar to that of benzoic sulphinide, the product in the case of para-toluic sulphinide being the acid ammonium salt of ortho-sulpho-para-toluic acid, the reaction by which it is produced being represented as follows:



The transformation of the acid ammonium salt into the acid chloride was brought about by mixing the dry, finely-powdered salt with about twice its weight of phosphorus pentachloride in a small Erlenmeyer flask, and shaking the two together. The reaction began immediately. After the evolution of acid fumes had to a great extent ceased, the flask was placed in a bath of sulphuric acid, and heated for some time at about 120° in order to be rid of phosphorus oxychloride. Unless this precaution be taken, there is likely to be loss in the subsequent washing with water, since the heat generated by the reaction of phosphorus oxychloride and water, will convert a large part of the acid chloride, in the presence of water, into the free acid, which is easily soluble. After the substance had been allowed to cool, the chloride was washed with cold water several times, and was then placed with a considerable amount of pure water in a flask connected with a reflux-condenser, and boiled until the oil had entirely disappeared. As this solution of the free acid was colored slightly yellow under these conditions, a little animal-charcoal was added and the boiling continued a short time. The solution, on being filtered and evaporated to dryness, to be rid of the hydrochloric acid formed in the reaction, redissolved, and again evaporated, yielded the crystallised ortho-sulpho-para-toluic acid.

The transformation of the acid ammonium salt into the free acid would be represented by the following equations:



Thus obtained, ortho-sulpho-para-toluic acid crystallises from concentrated aqueous solution in what appear to be tetragonal prisms terminated by planes belonging to the pyramid of the second order. The composition of the crystallised acid is represented by the formula  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{OH} \\ \text{CH}_3 \end{array} \right. + 3\frac{1}{2}\text{H}_2\text{O}$ , as is indicated by the analyses given below :

I. 0.1824 gram hydrous acid gave 0.2292 gram  $\text{CO}_2$  and 0.0866 gram  $\text{H}_2\text{O}$ .

II. 0.3029 gram hydrous acid gave 0.3874 gram  $\text{CO}_2$  and 0.1532 gram  $\text{H}_2\text{O}$ .

III. 0.2620 gram hydrous acid gave 0.2212 gram  $\text{BaSO}_4$ .

IV. 0.41165 gram hydrous acid gave 0.3520 gram  $\text{BaSO}_4$ .

Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{OH} \\ \text{CH}_3 \end{array} \right. ; \text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{OH} \\ \text{CH}_3 \end{array} \right. + 3\text{H}_2\text{O} ; \text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{OH} \\ \text{CH}_3 \end{array} \right. + 4\text{H}_2\text{O}.$			
C	44.44	35.55	33.33
H	3.74	5.185	5.55
S	14.85	11.85	11.11

Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{OH} \\ \text{CH}_3 \end{array} \right. + 3\frac{1}{2}\text{H}_2\text{O}.$		Found.			
		I.	II.	III.	IV.
C	34.41	34.28	34.88	...	...
H	5.38	5.275	5.62	...	...
S	11.47	...	...	11.59	11.74

Several attempts were made to determine exactly the water of crystallisation by heating the crystallised acid. The acid becomes anhydrous when heated for a long time at from  $135^\circ$ – $140^\circ$ . In each case, after the water had been driven off in amount closely approximating  $3\frac{1}{2}$  molecules, the anhydrous acid began to volatilise, as was evident from the white fumes evolved. The exact conditions necessary for dehydrating the acid without bringing

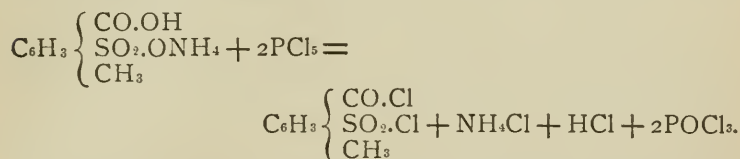
about volatilisation, were not found. The anhydrous acid melts at  $158^{\circ}$ .

Ortho-sulpho-para-toluic acid is dibasic, forming two sets of salts with metals. It is soluble in alcohol and in ether. It is also, in spite of the statement of Fittica to the contrary, very easily soluble in water. Its aqueous solution has to be quite concentrated before it will show signs of crystallisation. The solution, indeed, can be evaporated, without crystals separating out, to such a point that, when allowed to cool, the whole contents of the dish will become solid.

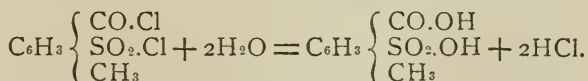
The crystals of the acid appear to be tetragonal, but on account of the rounding of the angles and the etching of the prismatic faces, due to its great solubility in water, a careful crystallographic study of the acid would have been impossible. The acid under some conditions is slightly efflorescent in the air, the clear-white crystals becoming opaque.

*Chloride of Ortho-sulpho-para-toluic Acid.*

In describing the preparation of ortho-sulpho-para-toluic acid, it was stated that the chloride of the acid is formed by the action of phosphorus pentachloride upon the acid ammonium salt of the acid, as indicated in the equation:



The chloride thus prepared is an oil whose melting-point is  $59^{\circ}$ . It is therefore solid at ordinary temperatures. It is purified by recrystallisation from "petroleum ether," and is thus obtained in crystals which are probably triclinic. It is easily soluble in ether and less readily in alcohol. Boiled with water it is transformed into the free acid and hydrochloric acid, according to the equation:



For the purpose of analysis 0.1720 gram of the acid chloride was heated with pure water in a sealed tube until the oil had entirely disappeared. The tube, when it had become cold, was

opened, the contents washed into a beaker, and the total amount of free acid present determined by means of a standard solution of ammonia. Since for each molecule of chloride decomposed one molecule of the dibasic acid and two molecules of hydrochloric acid are formed, one half of the ammonia added must have been employed in neutralising the hydrochloric acid. The quantity of the latter acid, and consequently the proportion of chlorine in the original chloride, may thus be readily deduced. Total quantity of ammonia solution required for neutralisation = 26.00 cc., which is equivalent to 0.0463 gram  $\text{NH}_3$ .

Calculated for $\text{C}_6\text{H}_3$ $\left\{ \begin{array}{l} \text{CO}_2\text{Cl} \\ \text{SO}_2\text{Cl} \\ \text{CH}_3 \end{array} \right.$	Found.
28.37	28.04

*Salts of Ortho-sulpho-para-toluic Acid.*

Salts of ortho-sulpho-para-toluic acid were prepared as follows: The neutral salts of potassium, ammonium, barium, calcium, magnesium, and silver; and the acid salts of potassium, ammonium, barium, calcium, and magnesium. The statement of Fittica<sup>1</sup> that the hydroxides of the alkali metals decompose the acid with the formation of sulphates, I have been unable to verify. The free acid, boiled with strong solutions of potassium, sodium and barium hydroxides, passes into solution without carbonisation or other signs of disintegration. The salts are stable. The silver salt does not give up its "water of crystallisation" until a temperature of  $215^\circ$  is reached, while the neutral calcium salt requires that the temperature be raised to  $260^\circ$  before it will become anhydrous. Even the *acid barium salt* is not rendered anhydrous until the temperature reaches  $235^\circ$ . The neutral potassium salt is not very rapidly decomposed by fused caustic potash. These facts certainly seem to show that it was not ortho-sulpho-para-toluic acid with which Fittica obtained these results.

The acid salts, as would be expected, are readily converted by boiling with metallic hydroxides or carbonates into neutral salts. No mixed salt of this acid was prepared, however, although compounds analogous to the silver-ammonium ortho-sulpho-benzoate,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO.OAg} \\ \text{SO}_2.\text{ONH}_4 \end{array}$ , prepared by Dohme and described in his dissertation, could in all probability readily be made.

<sup>1</sup> Ann. Chem. (Liebig) 172, 328-9.



Although it has not been proved, it will be assumed that in the acid salts the metal replaces the hydrogen of the sulphoxyl, rather than the carboxyl group, the general formula of these salts being,

therefore,  $C_6H_3 \left\{ \begin{array}{l} CO.OH \\ SO_2.OM, \text{ where } M \text{ represents an atom of any} \\ CH_3 \end{array} \right.$

univalent metal. The acid salts are as a rule less soluble than the neutral. All the salts prepared were clear and colorless, the silver salt, of course, turning dark if exposed to the light. On account of their extreme solubility in water, crystals of both acid and neutral salts were as a rule without well-defined edges. No attempts at crystallographic measurement were made.

*Neutral Salts of Ortho-sulpho-para-toluic Acid.*

*Neutral Potassium Salt,*  $C_6H_3 \left\{ \begin{array}{l} CO.OK \\ SO_2.OK + xH_2O. \text{—This salt} \\ CH_3 \end{array} \right.$

was prepared by simply neutralising a solution of the free acid by means of potassium carbonate solution. It is, like all the other neutral salts of ortho-sulpho-para-toluic acid with the exception of the silver salt, extremely soluble in water. A solution evaporated to the consistency of a syrup and placed over sulphuric acid in a desiccator, refused to crystallise, and after a month's time finally dried to a white, semi-crystalline crust. No analysis of the salt was made, but by fusion with caustic potash the sulphonic acid residue was replaced by the hydroxyl group, and ortho-hydroxy-para-toluic acid was formed. This reaction will be taken up for discussion later on.

*Neutral Ammonium Salt,*  $C_6H_3 \left\{ \begin{array}{l} CO.ONH_4 \\ SO_2.ONH_4 + 2\frac{1}{2}H_2O. \text{—This} \\ CH_3 \end{array} \right.$

salt is formed by boiling the solution of the acid ammonium salt with an excess of solution of ammonia. The boiling is continued until all excess of ammonia is removed. The salt is exceedingly soluble in water; the solution placed over sulphuric acid in a desiccator becoming concentrated to a syrupy condition before crystallisation begins, the salt being finally deposited as a crust on the bottom of the vessel containing it. Two analyses of the salt were made, the method being to decompose by means of caustic soda solution in a Kjeldahl apparatus. The ammonia given off was absorbed in a standard solution of hydrochloric

acid and the quantity determined by titration. The results obtained are expressed by the following figures:

I. 0.1942 gram of the salt gave 0.02237 gram  $\text{NH}_3$ .

II. 0.2549 gram of the salt gave 0.02954 gram  $\text{NH}_3$ .

		Calculated for			
		$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.ONH}_4 \\ \text{SO}_2.\text{ONH}_4 \\ \text{CH}_3 \end{array} \right. + 2\frac{1}{2}\text{H}_2\text{O}.$		I. Found. II.	
N		9.49		9.49	9.54

*Neutral Barium Salt*,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.O} \\ \text{SO}_2.\text{O} \\ \text{CH}_3 \end{array} \right\} > \text{Ba}$ .—This salt was made

by boiling a solution of ortho-sulpho-para-toluic acid with an excess of pure barium carbonate; and also by boiling a solution of the acid ammonium salt with an excess of the same reagent until no more ammonia was given off; filtering and evaporating to crystallisation. The salt forms fine, white needles which contain no water of crystallisation. The following results were obtained on analysing the salt:

I. The dry salt heated at  $190^\circ$  did not lose appreciably in weight.

II. 0.2706 gram of the salt yielded 0.1784 gram  $\text{BaSO}_4$ .

III. 0.39515 gram of the salt yielded 0.2611 gram  $\text{BaSO}_4$ .

		Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.O} \\ \text{SO}_2.\text{O} \\ \text{CH}_3 \end{array} \right\} > \text{Ba}.$			
				I. Found. II.	
Ba		39.03		38.77	38.85

*Neutral Calcium Salt*,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.O} \\ \text{SO}_2.\text{O} \\ \text{CH}_3 \end{array} \right\} > \text{Ca} + \text{H}_2\text{O}$ .—The method

of preparation of this salt was merely to boil a solution of the free acid with an excess of calcium carbonate in the form of powdered Iceland spar. After evaporating the filtered solution to a small volume and allowing it to stand several weeks over sulphuric acid in a desiccator, the salt crystallised in clear, colorless prisms, apparently monoclinic, extended parallel to the clino-pinachoidal faces. The crystals contain one molecule of "water of crystallisation," and hold it with such tenacity that the salt is not rendered anhydrous until a temperature of  $255^\circ$ – $260^\circ$  is attained. The anhydrous salt is very hygroscopic. The following figures were obtained on analysis:

I. 0.2772 gram of the salt yielded 0.1381 gram  $\text{CaSO}_4$ .

II. 0.2105 gram of the salt yielded 0.1044 gram  $\text{CaSO}_4$ .

III. 0.2304 gram of the salt, heated at  $260^\circ$ , lost 0.0154 gram in weight.

Calculated for				
$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO}_2\text{O} \\ \text{SO}_2\text{O} \\ \text{CH}_3 \end{array} \right\} > \text{Ca} + \text{H}_2\text{O}.$		I.	Found. II.	III.
Ca	14.71	14.65	14.58	...
H <sub>2</sub> O	6.61	...	...	6.63

*Neutral Magnesium Salt*,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO}_2\text{O} \\ \text{SO}_2\text{O} \\ \text{CH}_3 \end{array} \right\} > \text{Mg} + x\text{H}_2\text{O}.$ — This

salt is described by Fittica<sup>1</sup> as crystallising from absolute alcohol in yellow crystals without water of crystallisation, the color being probably due to impurity. The salt was prepared in the course of this investigation by boiling a solution of the free acid with magnesium carbonate, filtering and evaporating. Evaporated to dryness from aqueous solution, on the water-bath or in a desiccator, it hardens to a yellowish, gummy mass with no evidence of crystallisation. The same result was obtained from a solution in ordinary alcohol. The solution in absolute alcohol, however, on evaporation leaves a white, deliquescent paste—apparently a mass of fine, white crystals. I did not have time at my disposal to prepare this salt in proper condition for analysis.

*Neutral Silver Salt*,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO}_2\text{OAg} \\ \text{SO}_2\text{OAg} \\ \text{CH}_3 \end{array} \right\} + 1\frac{1}{2}\text{H}_2\text{O}.$ — This salt is

formed by boiling a solution of ortho-sulpho-para-toluic acid with an excess of silver oxide. The filtered solution, if not too concentrated, on cooling deposits the salt in the form of beautiful, strongly-refracting, colorless rhombohedra. If the solution be at all concentrated—and the salt is only slightly soluble even in boiling water,—instead of crystals, a yellow amorphous precipitate is obtained. The crystals are very slightly, if at all, soluble in cold water. They contain  $1\frac{1}{2}$  molecules of “water of crystallisation.” As would be expected, exposure to daylight renders the crystals dark-brown in color and opaque. In analysing this salt, the silver was determined as chloride, by precipitating by means of hydrochloric acid from a hot aqueous solution; and also as sulphate, by decomposing the compound by heating with strong sulphuric acid. These analyses gave the following results:

<sup>1</sup> Loc. cit.

- I. 0.4747 gram of the salt gave 0.2972 gram AgCl.  
 II. 0.3175 gram of the salt gave 0.2167 gram Ag<sub>2</sub>SO<sub>4</sub>.  
 III. 0.3761 gram of the salt, heated at 215°, lost 0.0225 gram in weight.

	Calculated for C <sub>6</sub> H <sub>3</sub> { CO.OAg SO <sub>2</sub> .OAg + 1½H <sub>2</sub> O. CH <sub>3</sub>	I.	Found. II.	III.
Ag	47.26	47.15	47.25	...
H <sub>2</sub> O	5.91	...	...	5.97

*Acid Salts of Ortho-sulpho-para-toluic Acid.*

*Acid Potassium Salt*, C<sub>6</sub>H<sub>3</sub> {  
CO.OH  
SO<sub>2</sub>.OK.—The method employed  
CH<sub>3</sub>

for the preparation of this salt, as well as of the acid barium and acid calcium salts, was that usually employed in preparing the acid salts of bibasic acids, *viz.* the acid solution was divided into two equal parts, one of which was neutralised by means of a carbonate, and the other then added. This salt forms ortho-rhombic prisms, when crystallised from water, and contains no water of crystallisation. On analysis:

- I. 0.5060 gram of the salt gave 0.1701 gram K<sub>2</sub>SO<sub>4</sub>.  
 II. 0.5530 gram of the salt gave 0.18595 gram K<sub>2</sub>SO<sub>4</sub>.

	Calculated for C <sub>6</sub> H <sub>3</sub> { CO.OH SO <sub>2</sub> .OK. CH <sub>3</sub>	I.	Found. II.
K	15.38	15.09	15.09

*Acid Ammonium Salt*, C<sub>6</sub>H<sub>3</sub> {  
CO.OH  
SO<sub>2</sub>.ONH<sub>4</sub>.—This salt is formed,  
CH<sub>3</sub>

as has before been stated, by the action of dilute hydrochloric acid upon para-toluic sulphinide. That the acid salt and *not* the free acid, is the product of this action, is certainly very interesting. The crystals of the salt are probably rhombohedral. Single crystals suitable for measurement are difficult to obtain, the tendency of the salt to form complicated crystal-aggregates being very marked. Treated with ammonia, the acid ammonium salt is converted into the neutral ammonium salt. Boiled with an excess of barium carbonate, ammonia is given off and the neutral barium salt formed. Phosphorus pentachloride converts this salt into the chloride of ortho-sulpho-para-toluic acid, as has been described. On analysis the following results were obtained:

I. 0.1812 gram of the salt gave 0.01307 gram  $\text{NH}_3$ .

II. 0.2272 gram of the salt gave 0.01607 gram  $\text{NH}_3$ .

Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{ONH}_4 \\ \text{CH}_3 \end{array} \right.$		Found.	
		I.	II.
N	6.01	5.94	5.83

The ammonia was determined by decomposing a known weight of the salt in a Kjeldahl apparatus by means of caustic soda solution, and fixing the ammonia given off with the aid of a solution of standard hydrochloric acid.

*Acid Barium Salt*,  $\left( \text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{O}- \\ \text{CH}_3 \end{array} \right. \right)_2 \text{Ba} + 4\text{H}_2\text{O}$ . — The method of preparation of this salt was the following: A solution of the free acid was taken, diluted to exactly 100 cc., divided into two portions of 50 cc. each, with one of which an excess of barium carbonate was boiled, and, after filtration, the other portion added and the solution evaporated to crystallisation. Most beautiful crystals in the form of long, perfectly colorless; clear needles, radiating from nuclei, were formed in the solution, but immediately on exposure to the air became opaque and crumbled to a white powder. The following results were obtained on analysing the salt:

I. 0.3310 gram of the salt gave 0.1210 gram  $\text{BaSO}_4$ .

II. 0.2713 gram of the salt gave 0.0989 gram  $\text{BaSO}_4$ .

III. 0.2713 gram of the salt lost 0.0310 gram in weight at  $235^\circ$ .

Calculated for $\left( \text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{O}- \\ \text{CH}_3 \end{array} \right. \right)_2 \text{Ba} + 4\text{H}_2\text{O}$		Found.		
		I.	II.	III.
Ba	21.44	21.50	21.43	...
$\text{H}_2\text{O}$	11.27	...	...	11.41

*Acid Calcium Salt*,  $\left( \text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO.OH} \\ \text{SO}_2.\text{O}- \\ \text{CH}_3 \end{array} \right. \right)_2 \text{Ca} + 4\text{H}_2\text{O}$ . — This salt

was prepared in just the same way as the corresponding barium salt, except that powdered Iceland spar was used instead of barium carbonate. The salt is very soluble in water, and crystallises from solution in thin cubical plates. The following are the results of analysis:

I. 0.1990 gram of the salt gave 0.0496 gram  $\text{CaSO}_4$ .

II. 0.2037 gram of the salt gave 0.0504 gram  $\text{CaSO}_4$ .



III. 0.1596 gram of the salt lost 0.0221 gram in weight on heating at 175°.

Calculated for				
$(C_6H_3 \left\{ \begin{array}{l} CO.OH \\ SO_2.O- \\ CH_3 \end{array} \right\})_2 Ca + 4H_2O.$		I.	Found.	III.
Ca	7.38	7.33	7.28	...
H <sub>2</sub> O	13.28	...	...	13.33

If heated above 175° the salt continues to lose weight, but shows at the same time evidence of more deep-seated decomposition.

*Acid Magnesium Salt*,  $(C_6H_3 \left\{ \begin{array}{l} CO.OH \\ SO_2.O- \\ CH_3 \end{array} \right\})_2 Mg + xH_2O.$ —The

method of preparation in the case of this salt was the same as that of the other acid salts, magnesium carbonate, however, being employed as reagent. It is almost as soluble in water as the corresponding neutral salt, yielding only a semi-crystalline crust on the bottom of the containing vessel after standing for more than a month over sulphuric acid in a desiccator. No analysis of the salt was made.

#### *Action of Caustic Potash on the Neutral Potassium Salt.*

In order to obtain still further evidence that the acid under investigation is that sulpho-para-toluic acid represented

by the formula  $C_6H_3 \left\{ \begin{array}{l} CO.OH \text{ (1)} \\ SO_2.OH \text{ (2)} \\ CH_3 \text{ (4)} \end{array} \right\}$ , the neutral potassium salt,

$C_6H_3 \left\{ \begin{array}{l} CO.OK \\ SO_2.OK \\ CH_3 \end{array} \right\}$ , was fused with caustic potash with the object

of forming, by the replacement of the sulphoxyl group by the hydroxyl group, an oxy-para-toluic acid. According to expectation, the acid formed should be that represented by the

formula  $C_6H_3 \left\{ \begin{array}{l} CO.OH \text{ (1)} \\ OH \text{ (2)} \\ CH_3 \text{ (4)} \end{array} \right\}$ . This acid and its derivatives have

been studied by Engelhardt and Latschinow,<sup>1</sup> Biedermann and Pike,<sup>2</sup> Oppenheim and Pfaff,<sup>3</sup> Ihle,<sup>4</sup> Iles and Remsen,<sup>5</sup> Jacobsen,<sup>6</sup> and Schall.<sup>7</sup> Its melting-point (uncorrected) is stated by Iles and Remsen to be 169°–170°; Jacobsen gives the temperature

<sup>1</sup> Ztschr. Chem. 1869, 623.

<sup>2</sup> Ber. d. chem. Ges. 6, 324.

<sup>3</sup> Ibid. 8, 889.

<sup>4</sup> J. prakt. Chem. [2] 14, 461.

<sup>5</sup> Ber. d. chem. Ges. 11, 462.

<sup>6</sup> Ibid. 11, 570.

<sup>7</sup> Ibid. 12, 820.

177° as the corrected melting-point. The acid is volatile with water-vapor. Its solution gives with ferric chloride a deep violet coloration.

Accordingly the dry neutral potassium salt was added to fused caustic potash, and the mass stirred until the salt had dissolved. After cooling, the contents of the crucible were dissolved in water and the solution acidified with hydrochloric acid, when a voluminous precipitate of white crystals was formed. These were filtered off, washed with cold water, dissolved in hot water, the solution boiled with a little bone-black, filtered, and the acid again crystallised, filtered out and dried. The melting-point as determined with the aid of a very accurate thermometer was 174.5°. The correction to be added to obtain the true melting-point was calculated and found to be between three and four degrees. This would give as the corrected melting-point 177.5°-178.5°. The acid is soluble in hot water with readiness; almost insoluble in cold water. It is volatile with water-vapor. The solution of the acid gives an intense violet color with ferric chloride solution. The appearance and behavior of the acid closely resemble those of its homologue, salicylic acid. The isomeric meta-oxy-para-toluic acid melts at 206°-207°. No salts of the acid were prepared.

#### *Para-toluic Sulphinide.*

The preparation of "methyl-saccharin," or para-toluic sulphinide, from para-toluidine has been already described. The substance as received from the manufacturers is a yellowish crystalline powder, only slightly soluble in cold water, quite easily soluble in hot; easily soluble in alcohol, less readily in ether. All the solutions of the substance, before treatment with bone-black, have a straw-yellow color. Determinations of the solubility in water of the *pure* sulphinide were made thus:

Two portions of 100 cc. each of a saturated aqueous solution (temperature = 15.5°) were evaporated to dryness. The residues weighed 0.1526 gram and 0.1491 gram respectively, the mean of which is 0.1508. This gives as the solubility of para-toluic sulphinide in cold water about 15 parts in 10,000.

Pure para-toluic sulphinide was prepared by boiling the hot aqueous solution with bone-black and filtering, when, as the solution cooled, the sulphinide separated in very fine white needles. If the solution be not saturated and if the cooling take place

slowly, these crystals attain a length of one or two inches, are about a twentieth of an inch in width, and are very thin and flat. They are probably monoclinic. Thus crystallised, the sulphinide

has the composition expressed by the formula  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right\} > \text{NH}$

+  $\frac{1}{2}\text{H}_2\text{O}$ , as is indicated by the results obtained on analysis:

I. 0.2989 gram of the sulphinide gave 0.5079 gram  $\text{CO}_2$  and 0.0928 gram  $\text{H}_2\text{O}$ .

II. 0.2292 gram of the sulphinide gave 0.3925 gram  $\text{CO}_2$  and 0.0803 gram  $\text{H}_2\text{O}$ .

III. 0.2307 gram of the sulphinide gave 0.01576 gram N.<sup>1</sup>

	Calculated for		I.	Found. II.	III.
	$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right\} > \text{NH}.$	$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right\} > \text{NH} + \frac{1}{2}\text{H}_2\text{O}.$			
C	48.73	46.60	46.33	46.71	...
H	3.55	3.91	3.45	3.89	...
N	7.11	6.80	...	...	6.83

As was the case with ortho-sulpho-para-toluic acid, the combustions were made by burning the substance with lead chromate and lead oxide according to the method devised by Mr. R. De Roode.<sup>2</sup> The nitrogen was determined by the Kjeldahl method. The same difficulty was met with in the case of the sulphinide as in that of the free acid when the attempt was made to determine the "water of crystallisation" by heating the substance and noting the loss in weight. Heated at  $190^\circ$  the sulphinide gradually loses weight, but as soon as the substance has been rendered anhydrous, that is, when the weight has been reduced by an amount closely approximating a half-molecule of water, the residue begins in part to volatilise and in part to decompose, as is rendered evident by the fumes given off and by the change in color of the residue.

Pure para-toluic sulphinide melts at  $249^\circ$ – $250^\circ$ . It possesses an intensely sweet taste, which is followed by a decidedly bitter taste after the sweet has disappeared. I have made no comparison of the intensity of the sweet taste of para-toluic sulphinide with that of benzoic sulphinide.

When heated in dry condition in a test-tube, para-toluic sulphinide sublimes to some extent, but the greater part decomposes with carbonisation.

<sup>1</sup> Mr. J. H. Holmes kindly made this determination for me.

<sup>2</sup> This Journal 12, 226.

*Salts of Para-toluic Sulphinide.*

Like benzoic sulphinide, para-toluic sulphinide is a monobasic acid, it being possible to replace the hydrogen atom of the imido group by the atom of a univalent metal. Three of these salts were prepared, *viz.* those of barium, calcium, and silver.

I. *Barium Salt*,  $\left( \text{C}_6\text{H}_3 \left\{ \begin{array}{c} \text{CO} \\ \text{SO}_2 > \text{N}- \\ \text{CH}_3 \end{array} \right\} \right)_2 \text{Ba} + 5\text{H}_2\text{O}$ .—This salt

was prepared by boiling a solution of para-toluic sulphinide with an excess of pure barium carbonate, filtering and evaporating. The salt crystallises very well, the form being triclinic. It is quite soluble in water. Analysis of this salt gave the following results:

I. 0.17355 gram of the crystallised salt gave 0.0649 gram  $\text{BaSO}_4$ .

II. 0.1938 gram of the crystallised salt lost 0.0281 gram in weight when heated for some time at  $145^\circ$ .

Calculated for $\left( \text{C}_6\text{H}_3 \left\{ \begin{array}{c} \text{CO} \\ \text{SO}_2 > \text{N}- \\ \text{CH}_3 \end{array} \right\} \right)_2 \text{Ba} + 5\text{H}_2\text{O}$ .		I. Found.	
		I.	II.
Ba	22.13	22.00	...
H <sub>2</sub> O	14.54	...	14.48

II. *Calcium Salt*,  $\left( \text{C}_6\text{H}_3 \left\{ \begin{array}{c} \text{CO} \\ \text{SO}_2 > \text{N}- \\ \text{CH}_3 \end{array} \right\} \right)_2 \text{Ca} + x\text{H}_2\text{O}$ .—When a

solution of para-toluic sulphinide is treated with powdered Iceland spar, the calcium salt is obtained. It is exceedingly soluble in water, as is the corresponding salt of benzoic sulphinide. Its aqueous solution deposits crystals when concentrated by evaporation and placed in a desiccator with phosphorus pentoxide. The crystals are opaque white needles. No analysis of the salt was made.

III. *Silver Salt*,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{c} \text{CO} \\ \text{SO}_2 > \text{N} \cdot \text{Ag} \\ \text{CH}_3 \end{array} \right\} + 1\frac{1}{2}\text{H}_2\text{O}$ .—This salt was

obtained by adding a solution of silver nitrate to a solution of para-toluic sulphinide. The greater part of the salt was deposited as a white precipitate, but, on standing, clear, diamond-shaped, colorless crystals were formed in the solution. The crystals possessed very marked refractive power. The salt probably has the composition given above, only one analysis having been made on account of the small quantity of the pure material at hand. The result of this analysis is the following:

0.10205 gram of the silver salt gave 0.0485 gram  $\text{Ag}_2\text{SO}_4$ .

Calculated for $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right\} > \text{N} \cdot \text{Ag} + 1\frac{1}{2}\text{H}_2\text{O}.$		Found.
Ag	32.63	32.68

*Anhydride of Ortho-sulpho-para-toluic Acid.*

Dohme, in his work upon the derivatives of ortho-sulphobenzoic acid, prepared the anhydride of the acid by heating the anhydrous acid with phosphorus pentoxide for a long time at  $130^\circ$ . In the hope of obtaining a similar derivative, some ortho-sulpho-para-toluic acid, which had been deprived of its water of crystallisation by heating for a long time at  $135^\circ$ – $140^\circ$ , was mixed with two or three times its weight of phosphorus pentoxide in a small flask through the stopper of which a piece of glass tubing was introduced, as recommended by Dohme, and the flask heated in a sulphuric-acid bath at  $145^\circ$ . The heating was continued twenty-four hours. At the end of that time the tube (which was of about one-half inch diameter) was lined with transparent white rhombohedra. The crystals were deliquescent; if exposed to the air, they rapidly became opaque and then dissolved in the moisture they had abstracted from the atmosphere. Heated with resorcin, a brilliant fluorescent substance was obtained. No analysis of the substance, which was probably the anhydride,

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CO} \\ \text{SO}_2 \\ \text{CH}_3 \end{array} \right\} > \text{O}$ , of ortho-sulpho-para-toluic acid, was made.

*Conclusion.*

The conclusions reached through the study of ortho-sulpho-para-toluic acid and its derivatives are the following:

I. The acid behaves in almost all ways like its homologue, ortho-sulphobenzoic acid, studied by Dohme.

It is very soluble in water, crystallising with three and a half molecules of "water of crystallisation," instead of four molecules.

It forms an anhydride similar to phthalic anhydride.

It forms two sets of salts, the acid and the neutral, the latter being as a rule extremely soluble in water.

The sulphinide, or anhydride of ortho-sulphamine-para-toluic acid, is, like benzoic sulphinide, a monobasic acid.

II. The statements of Fittica with regard to this acid show that, if he did obtain it at all, it was only in so impure a condition



that the actual properties of the substance were masked. He gives  $190^{\circ}$  as the melting-point of the anhydrous acid: I find that the acid becomes anhydrous at  $135^{\circ}$ – $140^{\circ}$ , and when in that condition melts at  $158^{\circ}$ . A sulphonic acid insoluble in water and instable toward bases, would certainly be regarded as a curiosity. The fact that strong oxidising agents convert ortho-sulpho-paratoluic acid into sulphuric acid as one of the products, as in the determinations of sulphur made by Pearson's method, would seem to indicate the possibility of the oxidation of thio-thymol by nitric acid beyond the desired stage, and the consequent formation of sulphuric acid. This would not, of course, explain the insolubility in water, which he ascribes to the product.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

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## THE ACTION OF LIGHT ON SILVER CHLORIDE.

BY ROMYN HITCHCOCK.

In a communication to the American Association for the Advancement of Science, at the Toronto meeting, 1889, I gave the results of some experiments which showed that, contrary to the general opinion of chemists, the chlorine set free from silver chloride by light amounts to not less than six per cent. of the weight of the chloride.<sup>1</sup> The accuracy of these results has been fully borne out by subsequent work, but it is doubtful if even my latest experiments, which show a loss of chlorine of over 8.5 per cent., have been carried far enough to represent the final effect of the light upon this compound. Indeed I may say almost with certainty that a still longer exposure of the films to sunlight would have shown a further loss. But I was obliged to stop my work quite suddenly and to leave undone several investigations which I had hoped to complete before publishing anything more upon this subject. The results here given are not to be taken as final; they are but a record of progress in a course of investigation which is

<sup>1</sup> This Journal **11**, 474.

of great promise, and which I hope to take up once more after my return from the far East.

The method of investigation is the same as that hitherto adopted. A very dilute solution of silver nitrate is precipitated in a dark room with dilute chlorhydric acid, and the finely-divided chloride allowed to settle upon slips of thin glass such as are used for covering microscopic objects. After about ten days the clear supernatant liquid is drawn off with a siphon, and replaced with distilled water run in very slowly by means of a siphon with an almost capillary end. In this way thin, quite perfect films of silver chloride were obtained. These were exposed to sunlight for many days and occasionally weighed. It was found that there was a constant decrease in the weight of the slips, which continued up to the final weighings, after at least one hundred days of exposure to sunlight.

The details of the manipulations are unimportant. It need only be said that the glasses were cleaned with sulphuric acid and potassium dichromate, and placed in a desiccator over sulphuric acid. They were then weighed several times, coated with the silver chloride in the manner described, and after thorough washing, again placed in the desiccator and weighed. They were then exposed to light under glass. In order not to confuse the reader with unnecessary figures, only a sufficient number of weighings will be given to indicate the progress of the decomposition. Only five slips, numbered as below, were used in the investigation. All the weighings were made on a fine Bunge balance, for the use of which I am indebted to the courtesy of Dr. Carl Barus.

Table I, showing the weights of the glass slips and of the silver chloride before exposure to light:

	Thin Glass, Average.	Glass + AgCl. Average.	Wt. of AgCl, Feb. 7.
I.	.41058	.43680	.02622
II.	.41051	.43437	.02386
III.	.41452	.44273	.02821
VI. <sup>1</sup>	.56131	.60112	.03981
IX. <sup>1</sup>	.63388	.67537	.04149

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Total AgCl, 0.15959

Table II, showing successive weights of slips after exposure to light:

<sup>1</sup> Slips VI and IX were of greater area than the others.

	Feb. 11.	Feb. 13.	Feb. 20.	July 12.	Aug. 25.
I.	.43576	.43542	.43529	.43504	.43491
II.	.43318	.43285	.43270	.43256	.43241
III.	.44143	.44098	.44083	.44053	.44041
VI.	.59948	.59882	.59858	.59764	.59743
IX.	.67401	.67342	.67306	.67181	.67130(?)

Table III, showing the loss in weight from the weighings in Table II, calculated for 0.1 gram AgCl:

	Feb. 11.	Feb. 13.	Feb. 20.	July 11 and 12.	Aug. 25.
I.	.00396	.00526	.00575	.00671	.00720
II.	.00498	.00637	.00700	.00758	.00821
III.	.00468	.00620	.00673	.00779	.00822
VI.	.00414	.00575	.00638	.00874	.00929
IX.	.00327	.00470	.00556	.00858	.00989(?)

A few words will explain some of the discrepancies noticeable in this table. Up to February 20th the slips were exposed to the sun in a small box with a glass cover. At that time it was observed that slips I and IX, which were at the ends of the box, were losing weight less rapidly than the others. The reason was that these two slips were partly shaded from the sun, mornings and afternoons respectively, by reason of their positions. The box was thenceforth discarded and the slips placed under beaker-covers. The last weighing of slip IX shows a loss greater than that due to the action of light—perhaps owing to mechanical injury to the film. This will be obvious if the weighings of the column of July 12th are compared with those of August 25th, for the loss of slip IX between the two weighings there appears more than twice as great as it should be. Rejecting this slip therefore, and also slip I as being below the truth for the reason given above, we may give the average loss in these experiments as 8.57 per cent. of the silver chloride used. This result is certainly well within the truth. The full extent of the decomposing action of light has not yet been reached. The course of dissociation is continuous during a long period of time, and can only be followed by the use of very finely-divided chloride spread in extremely thin films. It would be a rather surprising discovery, considering the literature of this subject, if it should be found that light effects the complete dissociation of silver and chlorine. But already one-third of the total chlorine is shown to be set free, and the process was certainly not complete.

Having observed such an unexpectedly large loss of chlorine in the manner described, it becomes of interest to know the composition of the resulting compound. This is a subject for more careful investigation in future, but as to first results I may say that warm dilute nitric acid dissolves from the exposed chloride a quantity of silver which corresponds to the amount of chlorine set free.

The bottom of the jar in which the slips were coated was more or less covered with the finely-divided precipitate. This was exposed to sunlight, then scraped off into a watch-glass and again exposed to the light for many days, with occasional stirring with a platinum wire. It was then weighed, treated with nitric acid and the silver determined in the solution. The results were as follows: AgCl darkened by light, 0.10141; AgCl from nitric acid solution, 0.03031, corresponding to Cl, 0.0075.

Not knowing the exact weight of the fresh, unexposed chloride used in this experiment, we cannot calculate the percentage of chlorine set free by the light, but the amount is obviously about 7 per cent. The analysis shows that the exposed and well-darkened chloride contains 22.5 per cent. of silver soluble in nitric acid—rather less than one-third the total amount of silver present in the pure chloride. But there is every reason to believe that the discolored chloride was still subject to the further action of light.

After the final weighing on August 25th, the five slips, which had been exposed to light for about four months, were placed in a beaker and digested with dilute nitric acid. The dissolved silver was determined as chloride, but before I could complete the analysis I was obliged to leave Washington. I am indebted to Dr. W. Hallock for collecting and weighing the precipitated chloride. The weight of silver chloride found by Dr. Hallock was 0.05588 gram, which is equivalent to 0.01382 of chlorine and 0.04205 of silver. From the weighings of August 25th we find the total loss of chlorine on the five slips to be 0.01393, which is perhaps excessive by reason of including slip IX, as already explained. This error, however, cannot well exceed three-tenths of a milligram, and is probably less. Comparing the results, we have: Loss of chlorine observed by weighings, 0.01393; chlorine calculated from silver dissolved by nitric acid, 0.01382. From this it would seem that the action of light is

merely to separate the chlorine from the silver, leaving the latter soluble in nitric acid, and it is of interest to observe that the quantity of silver thus rendered soluble is exactly equivalent to the weight of chlorine set free by the light.

Finally as a summary of results we have :

Original weight of AgCl, . . . . .	0.15959
Weight of Cl lost, . . . . .	0.01393
Per cent. of loss, . . . . .	8.57
Silver rendered soluble in HNO <sub>3</sub> , . . . .	0.04205

Composition of AgCl after action of light :

Weight of discolored AgCl, . . . . .	0.14566
Silver soluble in HNO <sub>3</sub> , . . . . .	0.04205
Per cent. of soluble silver, . . . . .	28.8

I am not much disposed to assign a formula to a compound of such very inconstant composition, but premising that I regard it only as a mixture of metallic silver and silver chloride, the proportions of these two constituents would be approximately represented by the formula (AgCl)<sub>2</sub>Ag.

S. S. PARTHIA, NEARING THE COAST OF JAPAN, *Sept.* 24, 1890.

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## NOTES.

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### *A New Optically Active Lactic Acid.*

While examining the water of a well for the *Anthrax bacillus*, Dr. Schardinger recently found<sup>1</sup> a micro-organism which, brought into a medium containing carbohydrates, caused active fermentation; if the liquid contains cane-sugar, the chief products of fermentation are alcohol and a lactic acid which turns the plane of polarisation to the right. According to the theory of LeBel and Van't Hoff concerning the optical properties of organic compounds, inactive ethylidene-lactic acid should be decomposable into two optically active isomers, as it contains an asymmetric carbon atom. Pasteur and Lewkowitsch found that

<sup>1</sup> Monatsh. Chem. 11, 545 (1890).



certain micro-organisms, brought in contact with inactive tartaric acid in a suitable culture-medium, destroy one half of the acid, and that the remaining half becomes laevo-rotatory. Lewkowitsch treated inactive phenyl-glycolic acid with the organism *Penicillium glaucum*, and this destroyed the laevo-rotatory half, leaving the dextro-rotatory intact. Lewkowitsch treated inactive ethylidene-lactic acid with this same organism, obtaining a dextro-rotatory variety identical with para-lactic acid. So, later, Maly, and Nencki and Silber found that other organisms feeding on inactive ethylidene-lactic acid left the dextro-rotatory, but till now a laevo-rotatory acid has not been known. The author's method of work was that of Fitz; he added to 1 liter water 30 grams sugar, 10 grams ammonium chloride, 0.2 gram magnesium sulphate, 1 gram disodium phosphate, and 15-20 grams calcium carbonate. This mixture, which has an alkaline reaction, was carefully sterilised by continued treatment in a current of steam. Then a pure culture of the organism was added, and the flasks containing the mixture kept from 12-14 days at 36°. In 24-36 hours fermentation was noticeable, and it reached its maximum on the fourth or fifth day, and ceased 7-8 days after. By evaporating the acid contents of the flasks to crystallisation, Scharfingher obtained a calcium salt of the new acid. 60 grams sugar yielded on an average 50 grams of this salt. By removing the calcium with oxalic acid and boiling the filtrate from the calcium oxalate with zinc carbonate, a zinc salt was obtained, identical in its chemical behavior and composition with zinc para-lactate. The free acid obtained from the zinc salt is a yellow, heavy, acid liquid, soluble in water, alcohol and ether. The silver salt was also made and analysed. The acid is laevo-, the salts dextro-rotatory, while para-lactic acid is dextro- and its salts laevo-rotatory.

If the new acid be mixed with a little alcohol or ether and allowed to stand in a desiccator over concentrated sulphuric acid, it loses water and becomes dextro-rotatory. Wislicenus has shown that para-lactic acid under similar conditions forms laevo-rotatory ester-anhydrides.

On mixing equal parts of solutions of the new zinc lactate and of zinc para-lactate, and evaporating, inactive zinc ethylidene-lactate crystallises out. The author has thus proved that inactive zinc ethylidene-lactate is made up of two optically active zinc lactates, and there can be no doubt that ordinary lactic acid consists of equal parts of dextro- and laevo-rotatory lactic acids, the case being analogous to that of tartaric and phenyl-glycolic acids.

E. RENOUF.

### *An Optically Active Glyceric Acid.*

The Journal of the Chemical Society for February, 1891, brings, under the above title, an article by Percy F. Frankland and Wm. Frew, describing an acid formed by the action on calcium glyce-

rate of a micro-organism called by them *Bacillus ethaceticus*, on account of its power to decompose mannite and glycerin into alcohol and acetic acid. Glyceric acid,  $\text{CH}_2\text{OH}-\text{CHOH}-\text{COOH}$ , contains an asymmetric carbon atom, and should, according to the theory of LeBel and Van't Hoff, be capable of existing in three isomers: the optically inactive form, and its components, the dextro- and laevo-rotatory forms. Hitherto, only inactive glyceric acid has been isolated, though Lewkowitsch, in his experiments with *Penicillium glaucum*, referred to in the preceding abstract, found that by growing this organism in a solution of ammonium glycerate the liquid became laevo-rotatory, but he did not follow up the investigation. Frankland and Frew find that when the *Bacillus ethaceticus* acts on a weighed quantity of the optically inactive calcium glycerate, under suitable conditions, it destroys one half of the salt, and the remaining half is laevo-rotatory. The pure acid obtained from the calcium salt was found to be dextro-rotatory. On heating aqueous solutions of the acid on the water-bath for some time, a white substance nearly insoluble in water is formed, which is powerfully laevo-rotatory. The authors believe this to be the anhydride of the acid, and consider the case analogous to that of the dextro-rotatory para-lactic acid and its laevo-rotatory ester-anhydrides as studied by Wislicenus. It now only remains to isolate in some way the laevo-rotatory glyceric acid, and from mixtures of the two optically active acids to build up the inactive variety, to complete the series of the glyceric acids demanded by the theory, as has been done with the series of tartaric, phenyl-glycolic and lactic acids.

E. RENOUF.

### *The Constitution of Benzene and Related Hydrocarbons.*

Julius Thomsen<sup>1</sup> has again applied thermic methods to the determination of the constitution of benzene and other ring compounds. Applying to trimethylene the formula  $f\text{C}_a\text{H}_{2b} = ax + 2by - \Sigma v + 0.58 \text{ C.}$ , in which  $x$  represents the heat of combustion of gaseous atomic carbon,  $y$  that of hydrogen attached to carbon, and  $\Sigma v$  the caloric value of the linkages or bonds, the calculated heat of combustion is found to agree with that found, only on the assumption that trimethylene contains three half-double bonds, or, in other words, that the union of the two carbon atoms in trimethylene is just one half as strong as the union of the two carbon atoms in ethylene. From this we may conclude that a "double bond" is really composed of two single bonds, which neutralise each other to a certain extent. Thomsen suggests this, and will probably test the hypothesis later.

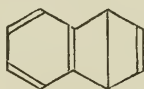
Applying the above formula to benzene, naphthalene, anthracene, phenanthrene and chrysene, it is found that the bonds have

<sup>1</sup> Zeits. für phys. Chem. **7**, 55.

different thermic values from those of gaseous aliphatic derivatives, and that the difference is not entirely due to the solid state of the aromatic compounds. Stohmann's figures are used, and as these are practically identical for anthracene and phenanthrene, these two compounds are considered as having equal numbers of single and double bonds, and are therefore treated as one. Benzene, naphthalene and chrysene are considered as belonging to one series, the others to another, as the difference between the heat of combustion of benzene and that of naphthalene is just one half the difference between the latter and that of chrysene, and the value obtained for anthracene varies perceptibly from the mean of the values of naphthalene and chrysene. It is easily seen, that if this is correct there must be more than one kind of linkage in these substances, and this conclusion is confirmed by the fact that the assumption of single bonds only leads to a greater heat of combustion for solid than for gaseous methane. Stohmann's figures are: Benzene, 777.3 C.; naphthalene, 1232.4 C.; anthracene, 1694.3 C.; phenanthrene, 1693.3 C.; chrysene, 2140.3 C.; and only by ascribing to benzene three, to naphthalene four, and to each of the others six double bonds, can Thomsen's formula be used. This gives the following graphic formulae:



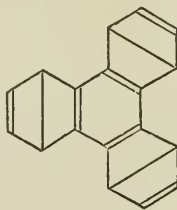
Benzene.



Naphthalene.



Anthracene.



Chrysene.

If the thermic value of a single linkage be expressed by  $v_1$ , and that of a double by  $v_2$ , we find that in gaseous aliphatic derivatives  $v_1 = \frac{x}{2} - 53.08$  C., and  $v_2 = x - 121.63$  C., in solid paraffin  $v_1 = \frac{x}{2} - 50.7$  C., and in solid aromatic compounds  $v_1 = \frac{x}{2} - 49.09$  C., and  $v_2 = x - 105.47$  C. The value of  $v_1$  varies but slightly, that of  $v_2$  greatly, and though the heat of combustion of a paraffin is increased 15.47 C. by the introduction of a double bond, that of an aromatic hydrocarbon is augmented but 7.29 C. If we adopt Thomsen's value for  $x$ , viz. 135.34 C., the values of  $v_1$  and  $v_2$  are

in olefines 14.59 C. and 13.79 C. respectively,  $v_1$  being the greater, and in aromatic compounds 18.58 C. and 29.87 C., the double bond being much the stronger and hence very different from the olefine double bond. 29.87 C. may also be considered as the sum of the values of two single bonds of unequal intensity, and benzene would then contain nine bonds, six of normal and three of abnormal value, the six stronger being the peripheral, the three weaker the centric linkages.

Thomsen seems not to have noticed the rather remarkable result which follows the acceptance of his value for  $x$ ,  $x = 135.34$ , and his formula for the thermic value of the triple bond,  $v_3 = \frac{3}{2}x - 203.18$ . If we substitute for  $\frac{3}{2}x$  its value 203.1, we get  $v_3 = 203.01 - 203.18 = -.17$ ; and if  $v_3$  is less than zero, it is difficult to conceive how the acetylene condition can exist. Hence there seems little doubt that  $x > 135.34$ , and that the heat-value of the reaction  $C, O = CO$  is greater than that of  $CO, O = CO_2$ .

F. LENGFELD.

### *Prof. Mendelejeff on Hydrazoic Acid.*

Interest in the remarkable discovery of Curtius<sup>1</sup> has been considerably heightened through the publication by Prof. Mendelejeff<sup>2</sup> of an essay which deals with the subject of hydrazoic acid and its relations to other compounds, in a broad way thoroughly characteristic of its author. In the following review the attempt will be made to bring forward the points of special interest in this paper.

If any element R form with a univalent element X<sup>3</sup> a compound  $RX_n$ , then R will form an hydroxide  $RO_{\frac{n}{2}}(OH)_{n-m}$ , in which, however, the number of oxygen atoms must not be greater than *four*. For it is a feature of the Periodic System that (1) the sum of the numbers representing respectively the highest valencies of the element toward hydrogen and toward oxygen shall be equal to *eight*; and that (2) the number of hydroxyl groups which a given element can retain in combination and still form a compound capable of isolation, is the same as the number of hydrogen atoms contained in the hydrogen compound of that element—if such a compound exist. Thus suppose an element R form a hydride RH; then the oxides of that element will have as limits the compounds  $R_2O$  and  $R_2O_7$ . If the hydride be  $RH_2$ , the oxides will be limited by that having the formula  $RO_3$ ; if  $RH_3$  or  $RH_4$ , then the oxides exhibiting the highest valency will be  $R_2O_5$  or  $RO_2$ , as the case may be. Besides, the hydroxides showing the highest valency, which exist in a free state, will be  $RO_3(OH)$ ,  $RO_2(OH)_2$ ,  $RO(OH)_3$  and  $R(OH)_4$ , respectively. It will be seen that the number of oxygen atoms in these hydroxides is never greater than *four*.

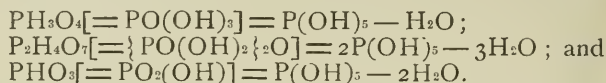
It therefore follows (1) that an element R, which—as is the case

<sup>1</sup> Ber. d. chem. Ges. 23, 3023.

<sup>2</sup> Ibid. 23, 3464.

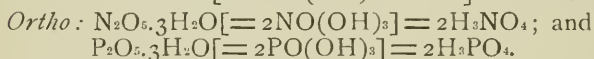
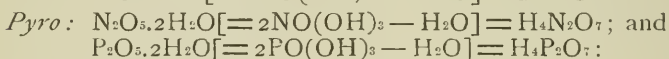
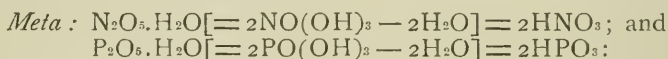
<sup>3</sup> Of course it will be evident that X cannot be *hydrogen*.

with nitrogen—forms a hydride  $RH_3$  and a highest oxide  $R_2O_5$ , cannot yield a hydroxide  $R(OH)_5$  which will exist in the free condition and form salts: it may, however, form a hydroxide  $R(OH)_3$ . On the other hand (2) the highest hydroxide which can yield salts is derived from that which we call the normal hydroxide, through loss of the elements of water: thus—



Finally (3) the ammonium salts characteristic of an element, being derived from these hydroxides, must contain other oxygen atoms in addition to those by means of which the ammonium radicle is held in combination. We thus have the salts,  $NO_2(OH)_4$ ,  $SO_2(OH)(OH)_4$ ,  $SO_2(OH)_2(OH)_4$ ,  $CO(OH)(OH)_4$ ,  $CO(OH)_2(OH)_4$ ,  $CHO(OH)_4$ , etc.

These ammonium salts, by loss of the elements of water, yield (1) amides and (2) nitriles. Thus ammonium formate,  $HCO(OH)_4$ , yields (1) formamide,  $HCO(NH_2)$ , and (2) hydrocyanic acid,  $HCN$ . Now since nitrogen and phosphorus form the hydrides  $NH_3$  and  $PH_3$ , respectively, the highest hydroxides which they can produce are—

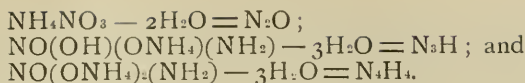


The normal acids, as, for example,  $N_2O_5 \cdot 5H_2O[=2N(OH)_5]$ , belong to the class of unstable compounds which may be considered to exist in the form of solutions.

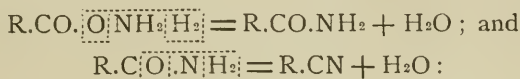
While on the one hand phosphorus forms with hydrogen a compound less stable than ammonia, so on the other hand its highest oxide is far more stable than nitric anhydride. Ortho-nitrates do not exist. Among the ammonium salts only the metantrate is known; still we can conceive of salts of the composition  $NO(OH)(OH)_4$  and  $NO(OH)_3(OH)_3$ , respectively—secondary and tertiary ammonium orthonitrates. These would yield amides,  $NO(OH)(OH)_4NH_2$  and  $NO(OH)_3(OH)_3NH_2$ : substances of the same composition as these two amides have been actually prepared through the action of dry ammonia gas on ammonium nitrate in solution.

By further abstraction of the elements of water from the amides, we might expect to obtain nitriles. Thus the nitrile of ammonium nitrate would be nitrous oxide; of the secondary and tertiary ammonium orthonitrates, hydrazoic acid and its ammonium salt, respectively:—

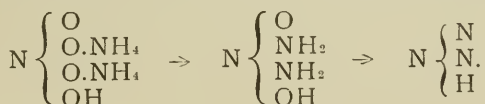




If we study the formation, from the ammonium salts, of the amides and nitriles of organic acids, we notice that one half the hydrogen in the ammonium radicle passes off with the oxygen atom which served to connect the ammonium radicle with the residue of the compound; and, when a further quantity of oxygen and hydrogen is eliminated, the hydrogen of the amido group passes out in combination with the oxygen of the carbonyl group; thus—



so, in the case of the formation of hydrazoic acid from secondary ammonium orthonitrate, the reaction may be thus represented :



The final product contains two nitrogen atoms originally combined with hydrogen in the form of ammonium radicles, and one which was originally contained in the nitric acid molecule: the hydrogen atom belonged to the acid residue, where it was present as hydroxyl, and consequently retains in hydrazoic acid its acid character. It is to be expected that, since nitrogen forms acids more energetic than those of carbon, the hydrogen of a nitrile of nitric acid will exhibit more marked acid properties than a corresponding derivative of an acid of carbon. On converting ammonium formate into formonitrile (hydrocyanic acid), the hydrogen atom, which in formic acid was not replaceable by metals, becomes acidic in the nitrile: there is reason therefore to look for very marked acid properties in hydrazoic acid. The greater acid-forming power of nitrogen, as compared with carbon, is seen when ammonia is contrasted with marsh-gas or ethane—the hydrogen of the ammonia is with much more ease directly replaceable by metals, as, for example, sodium. This we should be led to expect from a consideration of the relative position of the two elements in the Periodic System.

In this way Prof. Mendelejeff would explain the relative as well as the absolute acid-character of hydrazoic and hydrocyanic acids.

If now hydrazoic acid be a nitrile and, consequently, related to the cyanides, we should naturally look for some of the characteristic reactions of these compounds. Polymeric modifications of the acid or of its derivatives would be in order; the power to form double-salts corresponding to the ferrocyanides, etc., should

be noticeable; and the ability to pass over into isomeric relations—as ammonium cyanate goes over into urea—is conceivable. The power to polymerise is much more noticeable in the case of compounds of phosphorus than with compounds of nitrogen—the former element exists in several isomorphous modifications: in the gaseous state its molecule consists of *four* atoms; still it is probable that some trace of this peculiarity may be found in derivatives of hydrazoic acid. Phosphame, which is its phosphorus analogue, is believed to be represented by the formula  $(PN_2H)_n$ .

If double salts of iron and potassium can be made, then we ought to be able to obtain two series of compounds corresponding to the ferro- and ferricyanides, which would give characteristic colored salts, of which those analogous to the ferricyanides would, in all probability, be violently explosive, if indeed they could exist at all in the free state.

The unsymmetrical ammonium cyanate,  $CNO.NH_4$ , can be transformed into the symmetrical urea,  $CO.(NH_2)_2$ ; so, according to Mendelejeff, it may be possible to transform the unsymmetrical ammonium hydrazoate,  $N_3.NH_4$ , into the symmetrical diamide,  $N.NH_2.NH_2.N$ .

The author concludes with the hope that further investigation in this field will throw some light on what is really one of the darkest spots of the whole domain of chemical science—the chemistry of nitrogen.

WYATT W. RANDALL.

### *Hydrazoic Acid.*

Curtius and Radenhausen publish in No. 4 of the *Journal für praktische Chemie* for 1891 a brief article describing the properties of hydrazoic acid, which they have succeeded in obtaining pure. They say that the very explosive nature of the acid makes it impossible to study its physical properties carefully, and it is largely with the object of warning chemists against making the dangerous anhydrous acid that they publish this notice, which suffices to prove that the acid can exist in an anhydrous condition, and to characterise it. Hydrazoic acid or azo-imide,  $N_3H$ , is a colorless liquid, boiling without decomposition at  $37^\circ$ ; it mixes with water or alcohol, and has the terrible odor of the dilute acid intensified. It explodes in contact with heated substances, and sometimes without apparent cause at ordinary temperature, with unexampled violence, with evolution of brilliant blue light. Prof. Ostwald has studied the electrical conductivity of the acid, and thus finds it to be a somewhat stronger acid than glacial acetic acid. It is obtained by repeated fractional distillation of the aqueous acid. By this means a 91 per cent. acid was obtained, from which the remaining water was removed by calcium chloride. Hydrates, such as  $N_3H + H_2O$  or  $N_3H + 2H_2O$ , do not seem to exist.

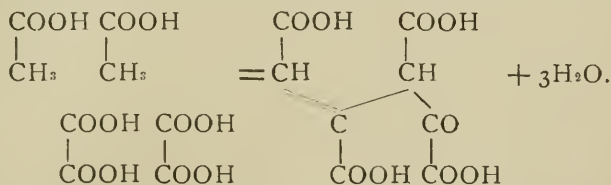
By placing 0.05 gram of the acid into the barometric vacuum at ordinary temperature, it exploded, reducing the apparatus to dust and scattering the mercury in extremely small particles to the most distant corners of the very large room. 0.7 gram of the acid exploded apparently without cause on lifting the tube in which it was contained from the freezing mixture. Mr. Radenhausen was seriously injured, and all the glassware standing near the place of explosion was shattered.

Curtius promises to make a careful study of the acid and its derivatives, as solutions of the acid and salts are not so explosive. Mendelejeff's prophecy<sup>1</sup> that nitrogen ammonium (ammonium hydrazoate),  $N_4H_4$ , would undergo molecular rearrangement is not confirmed by experiment. Curtius finds that ammonium hydrazoate is a substance crystallising in large, shining prisms; its properties are not changed by sublimation nor by boiling its aqueous solution; the crystals are not hygroscopic, but volatilise slowly at ordinary temperature, first losing their brilliancy and disappearing completely in a few days; but the last residues of the salt treated with mineral acids yield unchanged hydrazoic acid.

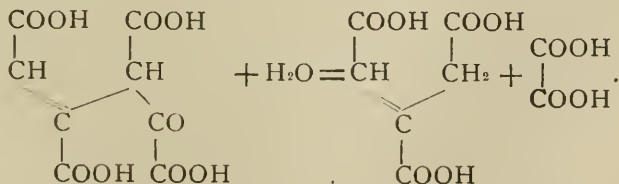
E. RENOUF.

### *Synthesis of some Organic Acids.*

Some interesting syntheses of acids occurring in plants are described by L. Claisen and E. Hori, in a recent number of the *Berichte*.<sup>2</sup> The syntheses are effected through the action of acetic acid on oxalic acid. These two acids may be conceived to act upon each other as shown below:



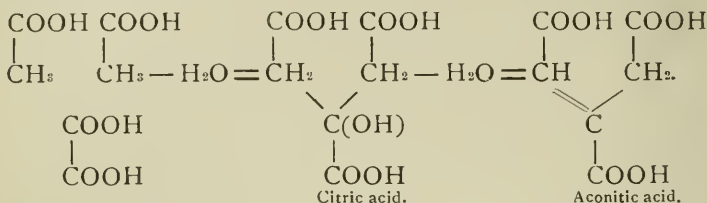
According to this, two molecules of acetic acid combine with two molecules of oxalic acid to form a tetrabasic acid which may be called *anhydro-diaceto-dioxalic acid* or *aconito-oxalic acid*, because it breaks down into oxalic and aconitic acids when treated with an alkali:



<sup>1</sup> Ber. d. chem. Ges. **23**, 3472.

<sup>2</sup> Ibid. **24**, 120.

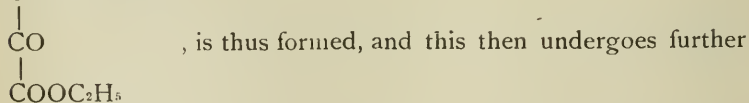
The synthesis of aconitic acid takes place easily at the ordinary, or at slightly elevated, temperature, so that we might almost believe that in nature the formation of aconitic as well as that of citric acid takes place in the same way. Salts of acetic and oxalic acids are present in most plants. Both acids might unite directly as follows:



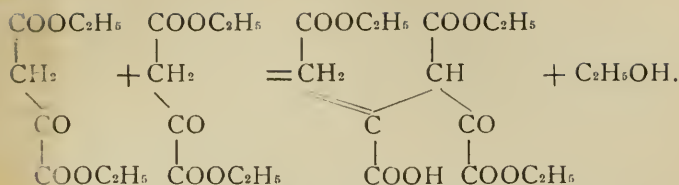
or they might first, and this appears to be the more probable view, unite to form *oxalacetic acid*,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{COOH}$ , from which the other plant acids could be formed. Under the influence of the reducing processes in the plants this oxalacetic acid would be partly converted into malic acid,  $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH(OH)} \cdot \text{COOH}$ , and, from this, asparagine,  $\text{CONH}_2 \cdot \text{CH}_2 \cdot \text{CH(NH}_2) \cdot \text{COOH}$ , could easily be formed; while, according to the investigations of Von Pechmann, asparagine itself probably serves as the starting-point in the formation of a number of the vegetable alkaloids. By the action of ammonia upon aconitic and citric acids also pyridine derivatives are easily formed, as has been shown by Von Hofmann and Ruhemann; and the vegetable alkaloids probably owe their origin to some extent to these reactions.

As regards the means by which these condensations may be brought about in the plants, the authors point out that potassium acetate, which is always present, is itself a powerful condensing agent, and that it has been used by Lieben in this capacity in numerous condensations.

The experiment, which suggests the above remarks, consists in treating a mixture of ethyl acetate and ethyl oxalate with sodium ethylate. An ethereal salt of the formula— $\text{CH}_2 \cdot \text{COOC}_2\text{H}_5$



condensation, the product being the ethyl ether of aconito-oxalic acid:



By treatment with an alkali the ether yields aconitic acid.

I. R.

*Resolutions adopted at a Conference of Chemists held in Philadelphia, December 30th and 31st, 1890, assembled to consider the formation of a national organisation.*

*Resolution 1.* It is desirable that an American Association of Chemists be formed to embrace all existing American Chemical Organisations.

*Resolution 2.* Resolved, that this Conference recommend to all existing American Chemical Organisations that they call a meeting of their bodies to be held in Washington in connection with the meeting of the American Association for the Advancement of Science for 1891, and that each of these organisations be requested to appoint a committee, or to continue their present committee for the further discussion of the subject submitted to the Conference now in session.

*Resolution 3.* Resolved, that this general Conference Committee, composed of the present sub-committees, or such others as may be appointed by the several organisations, be called together at as early a time as practicable before the joint meeting recommended in Resolution No. 2.

*Resolution 4.* Resolved, that meanwhile each sub-committee, through its chairman, by correspondence or otherwise, shall formulate such modifications of the Constitution of the American Chemical Society as it shall deem necessary to adapt it to the requirements of the Association proposed.

*Resolution 5.* Resolved, that the chairmen of these sub-committees shall then, so far as possible, harmonise the views embodied in these reports of their several organisations, and shall have printed for presentation at the joint meeting a report, or majority and minority reports, on a Constitution for the proposed Association of American Chemists.

Voted that the Chairman of this Conference, with Professor Clarke and Professor Hale, be a committee of three to select time and place for the meeting called for in Resolution No. 3.

Voted to request the American Chemical Society to print the minutes of this Conference with their report of the proceedings of the Philadelphia meeting, and to mail copies as widely as possible to chemists in North America.



The Secretary of this Conference is desired to communicate the above resolutions to scientific journals with a view to obtain a wide publication of the same.

Adjourned to meet at call of the Chair.

H. CARRINGTON BOLTON,  
*Secretary of the Conference.*

[The editor gladly publishes the above resolutions, and at the same time takes advantage of the opportunity to make a few comments on the subject of the proposed National Chemical Society. For many years past the subject has been discussed by the chemists of this country, and nearly twenty years ago an earnest effort was made to form an American society, with its headquarters at New York. For reasons which were almost entirely beyond the control of the gentlemen who were active in maintaining this organisation, it failed to become a national society in anything except its name. It is now proposed to try the same experiment, with Washington instead of New York as the headquarters. This has naturally awakened opposition on the part of the New York society, and it is, to say the least, doubtful whether the latter can be made to see the wisdom of the change. The writer ventures the prediction that, even if the New York society should yield its claims and become a section of the National Association, with headquarters at Washington, we should still have only a certain number of local societies, and should still lack the influence of a national organisation. The truth is, the conditions are unfavorable to the existence and usefulness of a national society in this country. There is no one place where there is a sufficient number of chemists of high standing to justify its selection as the headquarters of the society, and without some commanding section there would be something lacking. We have no London, no Paris, no Berlin. A section at Boston, or New York, or Philadelphia, or anywhere else would necessarily be local in its influence, and could not in any way control the society.

On the other hand, the writer is of the opinion that it would be a gain to chemistry to have some kind of an organisation that would bring the chemists of the country together more frequently. Such a society as the writer has in mind would not have any headquarters; its meetings would not be held for the sake of "papers"; it would not publish a journal; but it would furnish a good excuse for chemists to get together once or twice a year, and learn to know one another better. Hearty co-operation on some such basis as this would be of benefit. The editor will be glad to receive communications on the subject, and will publish in this Journal such as are appropriate, whether favorable or unfavorable to the general plan proposed.]

# AMERICAN CHEMICAL JOURNAL.

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## A SYSTEMATIC STUDY OF THE ACTION OF DEFINITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

BY WOLCOTT GIBBS, M. D., *Rumford Professor (Emeritus) in Harvard University*, AND EDWARD T. REICHERT,<sup>1</sup> M. D., *Professor of Physiology in the University of Pennsylvania.*

(Continued from p. 379, Vol. XII.)

### *Phenylhydrazine Chlorhydrate.*

In the frog, phenylhydrazine produces a diminution of sensation and reflex action, loss of voluntary motion, unconsciousness, and finally paralysis. The respirations and heart-beats are decreased. Death occurs from respiratory failure, and the heart is finally arrested in diastole. The nerves do not seem to be noticeably affected, the muscles are less excitable to electrical stimulus, and the cerebro-spinal centres are depressed. When given to dogs by the mouth in full doses there ensue, muscular weakness, unsteadiness in walking, depression of sensation and reflex action, nausea and vomiting, and increased rapidity in both pulse and respiration. The blood almost immediately becomes darkened, the mouth and conjunctiva having a marked appearance of cyanosis, which becomes more and more marked as the poisoning

<sup>1</sup> The appointment of Dr. H. A. Hare to the professorship of the Diseases of Children in the University of Pennsylvania obliged him to withdraw from the present investigation. His place has been supplied by Dr. Reichert, who has had exclusive charge of the purely physiological portion of the work remaining to be done.

progresses until the blood is almost black. The bodily temperature is lowered from  $1^{\circ}$  to  $2^{\circ}$  C. If a fatal dose was administered the weakness becomes profound, convulsive movements sometimes occur, sensation and reflex action disappear, the urine and feces are involuntarily voided, there is absolute muscular relaxation, respiration becomes slow and difficult, the pulse is weak, and finally death ensues from cardiac and respiratory paralysis.

When injected into the jugular vein in doses of 0.3 to 0.6 gram the arterial pressure is unaffected, the pulse is sometimes permanently decreased at once, and at others is decreased for a few minutes and then increased. The respirations are increased from one-half to three times the normal number. The blood is greatly darkened. After repeated injections of such quantities, the blood-pressure is invariably slowly and gradually diminished; the heart-beats are generally enormously increased in number, and the respirations are similarly affected. Death occurs in from fifteen to forty minutes, usually from heart-failure, although the respiration is profoundly affected and death may result from a cessation of this function or from a simultaneous arrest of both. If a single dose of from 1 to 1.5 grams is injected the pressure is immediately diminished, the heart-beats are enormously increased and very feeble, and death results in a few minutes.

The diminution of blood-pressure and the increase in the pulse are both due to a direct action on the heart, because the same changes are observed after the isolation of this organ from the nerve-centres, and as the fall of pressure is concomitant with the increased feeble pulse, the two changes progressing together. The increase in the pulse is not dependent on a depression of the inhibitory ganglion, since, even late in the poisoning, weak stimulation of the vagi causes marked inhibition; moreover, the more rapid beats are accompanied by lessened work, and are, therefore, significant of a direct depressant action on the heart-muscle. The increase in the number of respirations is present equally well after section of the pneumogastric nerves, and, consequently, is the result of an action on the respiratory centres. Whether this is direct or indirect through the action of the altered blood is also doubtful. Late in the poisoning, however, these centres are depressed, and may succumb before the heart.

The fatal dose in the dog when given by the mouth is from 0.20 to 0.25 gram to the kilo; when by the jugular vein, from

0.12 to 0.2 gram to the kilo. The fatal dose in the frog is about 0.0003 gram to the gram.

*Ortho-tolylhydrazine Chlorhydrate.*

In the frog this substance produces a diminution of sensation, loss of voluntary motion, slowing of the respirations and the pulse, and finally complete general paralysis. The nerves when tested by proper means do not seem to be appreciably affected, but the muscles are less irritable. The toxic actions are centred on the brain and spinal cord. Death results from a failure of respiration, and the heart is arrested in diastole.

When given to the dog by the stomach in doses of from 0.5 to 0.7 gram to the kilo of body-weight, it causes weakness, unsteadiness in walking, nausea and vomiting, bluish discoloration of the mouth and conjunctiva, and slight depression of sensation and reflex action. Bodily temperature is lowered; the respirations are increased, but towards the last they are slow, deep and difficult; the heart's action is slower and weak; convulsive movements of a clonic and tonic character occur; paralysis deepens; there is involuntary micturition and defecation; and death ensues from respiratory or cardiac failure. The heart is arrested in diastole, and the blood is almost black.

When injected into the jugular vein in doses of from 0.25 to 0.5 gram there is observed a slight increase in blood-pressure, which is usually accompanied by an unimportant increase in the pulse-rate. The respirations are unaffected or a little accelerated. After repeated doses, both pressure and pulse show a decided downward tendency, and the respirations become greatly increased. The arterial blood at this time is very dark, owing to the action on the hæmoglobin. As death approaches the respirations are diminished, the heart's action is very feeble, the pressure almost at zero, and finally death results from cardiac and respiratory paralysis. The alterations in both blood-pressure and pulse are observed even after the isolation of the heart from the nerve-centres, and as the changes in one are accompanied by corresponding alterations in the other, they must both be due to a direct action of the poison on the heart. The respiratory effects occur just the same after section of the pneumogastric nerves, and are therefore dependent upon an action on the respiratory centres. It is doubtful whether the poison acts directly on the respiratory

centres or not. The alterations in the blood are so profound that the increased respirations may be the indirect effect of the deficient oxygenising power of the red-blood corpuscles. The respiratory centres are, however, ultimately paralysed, as are all the nerve-centres.

The fatal dose in the dog when given by the mouth is from 0.3 to 0.5 gram to the kilo of body-weight; when by the jugular vein, from 0.2 to 0.3 gram to the kilo. The fatal dose in the frog is about 0.0003 to the gram of body-weight.

#### *Para-tolylhydrazine Chlorhydrate.*

The actions of para-tolylhydrazine are identical with those of the ortho salt, the only important difference being in a greater intensity of action of the former. The lethal dose was not accurately determined, but it is a little less than that of ortho-tolylhydrazine.

#### *Summary of the Physiological Actions of the Hydrazines.*

These substances all possess the same physiological actions in common. They powerfully affect the blood, converting the hæmoglobin into some abnormal form, and thus seriously interfere with the function of the red corpuscles as oxygen-carriers, which in turn acts as a depressant to all forms of vital activity and gives rise to a marked appearance of cyanosis; they depress the cerebro-spinal centres, causing loss of consciousness, sensation, and reflex action; they lower the bodily temperature, doubtless to a large extent by affecting the blood; they are all convulsants, yet relatively feeble in this respect; they all lower the blood-pressure and increase the pulse by a direct action on the heart; they arrest the heart in diastole; they increase the respirations and finally diminish them by primarily stimulating and secondarily depressing the respiratory centres; and they all cause death by cardiac and respiratory paralysis.

In point of general toxicity ortho-tolylhydrazine is least powerful, para-tolylhydrazine slightly more so, and phenylhydrazine half again more poisonous. These substances rank similarly in their actions on the heart, but the reverse is the case as convulsants, phenylhydrazine being feeble and para-tolylhydrazine the most potent. In a majority of cases with the tolylhydrazines the respiration will fail before the heart, but with the phenylhydrazines the heart will usually succumb first.



*Tolylene-diamine.*

After the injection of this substance into the posterior lymph-sac of the frog the animal soon exhibits signs of general depression: volitional movements become weakened, the legs are relaxed, the frog lies upon his belly, and, if placed on his back, makes no attempt to turn over, the motor reflexes are diminished and finally lost, respiratory movements cease, and the heart is arrested in diastole. The muscles are depressed, the sensory and motor nerves are not appreciably affected, and the loss of reflex excitability is due to an action on the spinal cord.

When administered to dogs by the mouth in the dose of 0.4 to 0.5 gram to the kilo of body-weight, there are observed: salivation, secretion from the nose, sneezing, retraction of the mouth with each inspiration suggesting difficult respiration, the tongue and gums are cyanotic, muscular movements are weakened, the heart-beat is more frequent and feeble, the respiratory movements may at first be increased but are always finally gradually diminished, the bodily temperature is lowered decidedly, the animal whines or howls occasionally as though in pain, the motor reflexes are greatly lessened, voluntary motion is lost, vomiting may occur, the reflexes are finally lost, and death ensues from a failure of respiration within from four to six hours after the dose.

Autopsies show that the blood is bluish-black, that the heart is arrested in diastole and full of dark clotted blood and unirritable, and that the stomach and intestines are greatly congested.

The subcutaneous injection of the drug gives rise to similar results during life and after death. Doses of a little over one half the quantity given above may prove fatal within twenty-four hours, the animals being profoundly affected for two or three hours, then recovering markedly, only to die later, apparently from gastro-enteritis.

Graphic records obtained of the actions on the circulation and respiration by means of the kymographion show that doses as small as 0.08 gram to the kilo injected intravenously are capable of increasing the pulse-rate, pressure and respiration. After doses of about 0.1 to 0.2 gram to the kilo the pulse-rate is variously affected, sometimes being unchanged, at others decreased, followed by a rise, and at others increased at once. After repeated doses the pulse is always increased. The effects on the pressure

are also variable, the general tendency at first being to cause a rise and afterwards a decline. The respirations after such doses are always increased. After repeated injections all three finally fail, death resulting from an arrest of respiration, but the heart is seriously depressed and arrested in diastole.

After section of the vagi and the upper cervical portion of the spinal cord the changes in the circulation are precisely the same as in normal animals, showing, therefore, that the effects on the pulse and pressure are due to direct actions on the heart. The primary increase and final decrease in the respiration-rate are observed after section of the pneumogastric nerves, and are, as a consequence, dependent upon actions on the corresponding centres.

The minimum lethal dose in dogs, when given subcutaneously, is from 0.2 to 0.3 gram to the kilo. Much larger quantities may be intravenously injected without causing immediate death.

#### *Di-nitro-phenol.*

When di-nitro-phenol is injected into the jugular vein of a dog in the dose of from 0.01 to 0.17 gram to the kilogram of body-weight, very marked and powerful stimulation of the vagi nerves always occurs, causing a very slow pulse with full systolic waves. This stimulation of the vagi is in direct ratio to the amount of the drug given, and seems to vary slightly with the susceptibility of the individual animal. Following this stage, if the dose has been as small as from 0.01 to 0.025 gram to the kilo, there comes a period of increased pulse-rate of a not very marked character, accompanied by a rise in blood-pressure.

These changes occur in both curarised and non-curarised animals, and are constant. We have further proved by repeated experiments that the slow pulse is due to vagal stimulation of a centric nature, since it is at once put aside by section of these nerves, the pulse-rate becoming as rapid as in the normal dog under such circumstances.

When as much as 0.170 gram to the kilo is injected into the jugular vein, the heart stops before respiration ceases, becoming slower and slower, until finally the arterial pressure also begins to fail and death occurs. Death is produced by as little as 0.05 gram to the kilo.

When di-nitro-phenol in the dose of 0.3 gram to the kilo is

given to a full-grown dog by the mouth in 40 cc. of water, vomiting comes on in from 5 to 10 minutes, which soon rids the stomach of the drug. For this reason the exact dose necessary to produce the symptoms which follow cannot be stated. The tongue is protruded and saliva drips from the mouth and from the end of the tongue; the respirations are greatly increased, becoming exceedingly frequent, as high as 180 per minute, but full and forcible, the chest-walls being distended to the utmost at each breath. The head is extended to straighten the windpipe, the pace is slightly staggering, and the hind legs are a little more affected than the fore. Consciousness is entirely preserved. The pupils are widely dilated, the temperature in the rectum rises from  $2^{\circ}$  to  $3^{\circ}$  C. Thirst soon becomes severe, probably owing to the rapid respirations. Death ensues in a half an hour, the respirations suddenly becoming slower and slower, then ceasing at once. After death *rigor mortis* appears immediately. Sometimes the urine and feces are passed involuntarily late in the poisoning. The urine is colored yellow, probably from the drug.

When 0.166 gram is given for each kilogram the symptoms are identical with those just stated, except that death is put off for one hour and a half. Shortly before death the animal emits a few howls, walks around the room, and then lying down suddenly ceases breathing. The heart at first is slowed in its beat, afterwards the action becomes very rapid, finally reaching 190 a minute. It was noted that respiration stopped before the heart.

When di-nitro-phenol in the dose of 0.015 gram is given to a frog weighing 80 grams, the drug being injected into the posterior lymph-sac, the hind legs seem to have their power slightly decreased, but rapidly recover their normal tone after a few minutes. Soon after this, about fifteen minutes following the injection, muscular power progressively diminishes, and the animal, when placed on his back, has great difficulty in regaining his proper position. Twenty minutes after the dose was given the frog is very much relaxed and appears half dead, so that he will lie in any position in which he is placed. Every portion of the body is discolored by the poison. Five minutes later the reflexes are still intact. Respiration ceases, and on exposing the chest at this time the heart is found to be acting with a remarkable degree of slowness, the diastole being long and the relaxation great. The blood is seen to be dark and grumous. Forty minutes after the drug

was given the beat is only 10 or 12 per minute, and the animal, now having lost all reflexes, is to all appearances dead, save for the occasional heart-beat. The question at once arises as to the cause of the failure of motor power and the subsequent loss of reflex activity. In order to determine whether the drug acts on the spinal cord, or on the nerves, or muscles, the artery of one hind leg was tied, thus preventing the access of the poison to the part thus supplied by the vessel, and the drug was then injected into the posterior lymph-sac. As the minutes pass by it is noted that the reflexes remain equal in both the protected and unprotected legs, which is followed by a loss of power in the entire body, with a complete loss of reflex activity in all parts alike. Respiration has ceased. No response can be obtained by any form of mechanical or chemical stimulus. On opening the chest the heart will be seen beating only about once a minute, and finally only the auricles contract.

This substance must act upon the spinal cord, and its action is doubtless chiefly on the motor portion, for the reasons that there is an equal failure of power in both protected and unprotected legs, which would not be the case if the action were peripheral; and because the impulses arising from peripheral irritation seem readily carried up the sensory part of the cord at a time when the general condition is one of profound muscular relaxation.

It is worthy of note that death occurs from respiratory failure if the dose be slowly absorbed as when given by the stomach, but from heart-failure if it be injected into the jugular vein in a single dose.

#### *Tri-nitro-phenol.*

When about 0.06 gram of this substance to the kilogram of the dog's weight is injected into the jugular vein there immediately ensues an extraordinary stimulation of the pneumogastric nerves or centres, so that the heart is within a few seconds completely arrested. At this time, however, section of these nerves restores the cardiac action, so that it would seem that the action of the drug is upon the central portion of the inhibitory apparatus of the heart. It is evident, however, that the peripheral portion is also acted upon, because the normal rate is not restored. This is corroborated by the fact that atropine, if injected at this time, fails to increase the rate at all. Tri-nitro-phenol seems to prevent the action of atropine on the ends of these nerves. Along with

the slowing of the heart's action there is a slight and constant fall of arterial pressure. If the dose be only 0.03 gram to the kilo these effects are less marked.

Upon the respiration the drug acts as a depressant, a dose of 0.06 gram to the kilo being fatal in this way. As a consequence, should further studies be necessary the animal must be kept alive by artificial respiration.

When 0.00001 gram to the gram is given to a frog and injected into the posterior lymph-sac, it causes a slight increase in the reflexes, which is accompanied by a slowing of the heart. If the dose equals as much as 0.000017 gram to the gram these symptoms are somewhat increased, and death ensues many hours afterwards from respiratory failure. If the dose is increased to 0.00005 gram to the gram the reflexes are at first increased, then diminished, and simultaneously the respiratory movements become much embarrassed and slowed, death eventually resulting from respiratory paralysis. The pulse is also much slower. After 0.0001 gram to the gram is given, absolute and complete paralysis comes on, and there is no stage of increased reflex activity as occurs with smaller doses. After death the nerves and muscles respond more feebly to electrical stimulation than normal. The minimum fatal dose of tri-nitro-phenol is 0.000015 gram to the gram of the frog, death being due to respiratory paralysis accompanied by cardiac depression.

Erb found that the daily use of a grain of this substance for ninety days in a rabbit produced yellowness of the conjunctiva, of the inner surface of the ear, and of the urine, with an occasional slight diarrhœa and great loss of weight, without any elevation of temperature. After a time the animal seemed to grow accustomed to the poison, so as to regain in great measure its flesh. Three grains a day caused, in about two weeks, the death of the rabbit, with symptoms of inanition. All the tissues, except the nervous, were stained of an intense reddish color, as was also the urine. Eight grains produced a fall of temperature, weakness, diarrhœa, collapse and death, sometimes preceded by tremblings and even by convulsions, in about twenty-three hours. The most remarkable physiological effect of the poison occurred in the blood. The blood of animals slowly killed by the poison was of a dirty brown color, with distinct nuclei both in the red-blood disks and floating free in the serum. Dr. Erb found that this alteration



occurred during life, and was accompanied by a decided increase in the number of white corpuscles. These changes in the blood were apparently the cause of death, and seem to have been due, so far at least as concerned the red disks, to a direct action, for Erb found that identical, or very similar alterations took place when the blood was mixed with the picrate of sodium outside of the body.

Erb found picric acid to act on man as on the lower animals. Twenty-four hours after the ingestion of fifteen grains of it the yellow color was plain in the conjunctiva, the skin and urine. The temperature was not elevated, and gastric disturbance was usually absent, but sometimes it was severe. As in animals, so in man, picric acid was found abundantly in the urine. A teaspoonful produced no more violent symptoms in man than bad vomiting and purging.<sup>1</sup>

*Summary concerning the Actions of the Nitro-phenols.*

*Ortho-nitro-phenol* kills by cardiac arrest when given by the jugular vein, and by respiratory failure when administered by the mouth. Death is produced by 0.1 gram to the kilo of body-weight. The cardio-inhibitory apparatus is stimulated centrally and peripherally.

*Meta-nitro-phenol* kills by cardiac failure when given by the jugular vein, and by respiratory paralysis when by the mouth. Death is produced by 0.083 gram to the kilo by the jugular vein. The cardio-inhibitory apparatus is stimulated the same as by the ortho compound.

*Para-nitro-phenol* is fatal by heart-failure when given by the jugular vein, and by respiratory arrest when by the mouth. Death is produced by 0.01 gram to the kilo by the jugular vein. The cardio-inhibitory centres and peripheries are stimulated by small doses, but large doses paralyse them.

All three affect the nervous system, slightly depressing it.

*Di-nitro-phenol* kills by heart-failure when administered by the jugular vein, and by respiratory paralysis when by the mouth. Death is caused by 0.05 gram to the kilo by the jugular vein. It powerfully stimulates the cardio-inhibitory apparatus. The nervous system is depressed in its motor portion.

*Tri-nitro-phenol* kills by respiratory failure unless the drug is thrown into the circulation in large amount *en masse*, when it

<sup>1</sup> Wiener Med. Presse 23, 1526.

arrests the heart. Death is produced by 0.06 gram to the kilo when injected by the jugular vein. It stimulates the cardio-inhibitory centres with extraordinary power.

*Nitro- and Di-nitro-benzol.*

*Nitro-benzol.*—In the frog this substance induces a brief period of reflex excitability, during which convulsive movements may occur; this is followed by weakness and gradual loss of reflex excitability. The respirations and heart-beats are increased, voluntary movement is soon abolished, the respirations cease, and finally the heart succumbs. Convulsions rarely occur, and when present are of spinal origin. The sensory and motor nerves and muscles are little, if at all, affected, so that the changes in reflex excitability are of spinal origin. The blood is of a chocolate color.

When administered to the dog by the stomach, in the dose of 0.5 to 0.75 gram to the kilo of body-weight, there is observed, salivation, vomiting, decided restlessness, unsteadiness in walking and other movements, staggering, tremors, delirium, an increase of temperature, a rapid pulse, and an increase in the respirations. As the toxic actions progress, weakness in the legs is marked, the animal is unable to stand, and crawls upon his belly or lies upon his side, making ineffectual attempts to get on his feet. Unconsciousness supervenes, the dog barks, whines or howls occasionally, and convulsive movements may occur of a clonic and tonic character. If vomiting has not been observed, the climax of the toxic action is reached within two hours, and apparent recovery occurs in from four to six hours. Should the dose be as large as 1 gram to the kilo, the dog gradually passes into a condition of paralysis of all the functions, the circulation fails, the blood may be more or less chocolate-colored or unaffected, the respiratory centres are depressed, and death results from their paralysis. The alterations in reflex excitability and the convulsions are due essentially to a direct action on the spinal cord.

The degree of poisonous action does not depend regularly upon the size of the dose, the same proportionate quantity in different animals causing wide variations in the intensity of action. Moreover, doses sufficient to cause marked and immediate effects when given by the stomach, are practically inert when injected subcutaneously. Even as much as 0.75 gram to the kilo may thus be given without other obvious effects than a slight increase of the

pulse, slight tremors, and restlessness. Doses of 2 grams to the kilo subcutaneously may elicit within six hours no other symptoms, the toxic actions progress very slowly, and the animal passes into a moribund condition, and may remain this way for twenty-four hours or more before death ensues.

When injected into the external jugular vein in doses of 0.5 to 1 gram the arterial pressure is diminished, and the pulse and respirations increased. Repeated doses lower the pressure more and more, the increase of the pulse is followed by a decrease, but the respirations tend to become greatly augmented. The increase in the heart-beats is usually trifling and transient, although in some cases it persists until death. Both the increase and decrease in the pulse indicate cardiac depression, since both occur after the isolation of the heart from the nerve-centres, and as they are always accompanied by lowered arterial pressure, which is in part independent of any vaso-motor action. While the fall of arterial pressure is chiefly due to a depression of the heart, the vaso-motor centres in the medulla oblongata are also involved, since this effect is not as decided after their destruction. The changes in the respirations are due to a direct action on the respiratory centres, because they are observed equally well after section of the par vagum. The blood may not in the least be discolored unless the action of the poison has extended over several hours, but the spectroscope invariably shows the presence of nitrite-hæmoglobin.

Death invariably results from a failure of respiration, although the circulation and other important functions are seriously depressed.

The lethal dose in the dog by the stomach is from 0.75 to 1 gram to the kilo of body-weight; and by the vein, from 0.15 to 0.25 gram to the kilo in divided doses. Absorption takes place so slowly from the subcutaneous tissues, or for some other obscure reason, that the fatal dose by this means is disproportionately large.

*Di-nitro-benzol.*—The physiological actions of this substance do not, as a whole, differ essentially in character from those of nitro-benzol, save in intensity. This preparation is more apt to cause vomiting; it is rapidly absorbed from the subcutaneous tissues, and is consequently quickly poisonous when given in this way; its action on the respiratory centres is very feeble as a stimulant but strong as a depressant, so that the respirations are usually but

little increased and generally notably decreased; the actions on the spinal cord are far more pronounced, the alterations in reflex excitability are more decided, and convulsions are almost invariably observed which are of a strong tetanic nature; the heart and vaso-motor centres are more depressed; the blood is always greatly discolored, and so marked is this in comparison with what is observed in poisoning with nitro-benzol, that one generally can tell simply by the color of the blood which substance was used—in poisoning from nitro-benzol the blood may not in the least be discolored, but even small doses of di-nitro-benzol will make themselves strongly manifest in this way; finally, it acts more promptly and powerfully, and is lethal in smaller doses.

### *Amides.*

*Formamide.*—In the frog this substance causes a diminution of sensation, muscular twitchings, clonic convulsions followed by those of a tonic character, paralysis, and finally death from respiratory failure. The sensory and motor nerves do not seem to be affected, for they retain their irritability long after death. The convulsions, as well as the diminution of sensation, are due to actions on the spinal cord.

When given to the dog by the mouth it so readily produces vomiting that the drug is ejected before any definite symptoms are developed. If injected subcutaneously in doses of 2 grams to the kilo of body-weight, it gives rise to restlessness and signs of pain, which are evidently due to the local irritation caused by the formamide. Vomiting is apt to occur, the bodily temperature is diminished, and the pulse somewhat slower.

When injected into the jugular vein in doses of from 0.2 to 0.3 gram to the kilo there is a momentary fall of blood-pressure, but no decided change in the pulse-rate. This diminution, which amounts to from an eighth to a fourth of the normal pressure, is followed in a few moments by a recovery, so that the normal is attained within about thirty seconds. The pressure continues to increase, and it may reach from ten to forty millimeters in excess of the normal. This increase is accompanied by a marked slowing of the pulse and vigorous heart-beats. The pressure gradually returns to the normal, but the pulse continues at a lessened rate. The respirations are also slower. When these doses are repeated similar results follow each injection, until after awhile the pressure

is permanently lowered, the heart's action excessively slow and strong, the respirations decreased, and death results from paralysis of respiration. When larger doses are given the circulatory and respiratory changes are intensified.

The slowing of the pulse is due to a stimulation of the cardio-inhibitory centres in the medulla oblongata, since it is not observed after section of the vagi. At the approach of death the heart-beats are also decreased, but this is of cardiac origin, because it is present even after the isolation of the heart from the nerve-centres. The changes in blood-pressure are essentially vaso-motor, and due to a direct action on the capillaries. This is evident in the facts that they occur after the destruction of the vaso-motor centres in the medulla oblongata and the separation of the heart from the nerve-centres, and as they are not accompanied by corresponding alterations in either the number or character of the heart-beats. The slowing of the respirations is the same after the pneumogastric nerves are cut, and is, therefore, the result of a depression of the respiratory centres.

The fatal dose in the dog when given by the jugular vein is from 1.5 to 2 grams to the kilo of body-weight. In the frog the fatal dose is about 0.0003 gram to the gram.

*Acetamide.*—Upon the frog, acetamide in the dose of 0.0005 gram to the gram causes great quietude, relaxation, and depression of respiration. If the dose be as large as 0.001 gram to the gram these symptoms are followed by an increase in reflex action, and then by convulsions of a tetanic type which are of spinal origin.

Given to the dog by the mouth in the dose of 0.5 to 0.7 gram to the kilo it is likely to cause vomiting, but no other troubles. Even doses of 2 grams to the kilo are without important effects.

When injected directly into the circulation in doses of from 3 to 5 grams the pressure is slightly increased, the pulse lowered from ten to twenty beats, and the respirations a little increased. These doses may be repeated until the animal receives a quantity equal to 3 grams to the kilo without increasing the pressure more than ten millimeters and the respirations more than one-third, or diminishing the pulse more than one-fifth. The slowing of the pulse we have determined to be due to a stimulation of the cardio-inhibitory centres.

These large doses seem to cause pain when they are injected, and also induce more or less struggling. After a time there is



produced extreme drowsiness or deep sleep. The animal's temperature does not appear to be affected.

The lethal dose for the dog is not known to us, but it is more than 5 grams to the kilo. The fatal dose in the frog is about 0.002 gram to the gram.

*Propionamide*.—When given to the frog in the dose of 0.004 gram to the gram, loss of voluntary movement rapidly ensues, and this is followed by tetanic convulsions. The nerves and muscles readily respond to stimulus long after death. The convulsions are spinal.

When given to the dog by the stomach or jugular vein, the animal being free to run about, it produces no symptoms other than a slight increase in the respirations and a slowing of the pulse. Doses as high as 0.5 gram to the kilo are thus ineffectual. When the dose is 0.05 gram to the kilo by the vein no change in arterial pressure occurs, and the pulse is not affected in either rate or force. Even if the dose amounts to 0.125 gram to the kilo there is little effect, but if it is as much as 0.25 gram to the kilo the pulse is much slower and the beat decidedly stronger, and the blood-pressure is increased. The decrease in the pulse we have found is due to a stimulation of the cardio-inhibitory centres.

The fatal dose in the frog is about 0.0005 gram to the gram.

*Benzamide*.—Upon the frog in the dose of from 0.003 to 0.005 gram to the gram it causes a diminution of sensibility and reflex action, loss of voluntary movement, and paralysis. The nerves and muscles do not seem to be affected, but the spinal cord is certainly depressed.

If administered to the dog by the mouth in the dose of 0.8 gram to the kilo of body-weight it induces staggering, salivation, vomiting, muscular weakness, diminution of sensibility and reflex action, a lowering of bodily temperature from  $1^{\circ}$  to  $3^{\circ}$  C., an increase in the respirations, a decrease in the pulse, profound relaxation, and unconsciousness. If the drug has not been lost by vomiting the pulse becomes feeble, the respirations slow, and death results from a failure of respiration.

When injected into the jugular vein of the dog in doses of 0.5 gram to the kilo the blood-pressure rapidly declines for about thirty seconds until it reaches a point fifty or sixty millimeters below the normal; the pulse at the same time is more frequent and the force of the heart-beat lessened, and the respirations are

increased in frequency and depth. The pressure, when it reaches its lowest point, immediately begins to recover; the pulse at the same time becomes slower and in a few minutes is less than normal, but the force of the heart is increased, although not sufficient to restore the normal pressure; and the respirations are slower and deeper. When this dose is repeated similar results ensue from each injection until the pressure is permanently lowered almost to zero. Even now several doses may be given before the heart is paralysed. Three doses are sufficient to abolish completely all sensation and to dilate the pupils. Death usually results from a failure of respiration.

The alterations in the pulse-rate are observed after the isolation of the heart from the nerve-centres, and are, therefore, due to a direct action of the poison on the heart. The diminution of blood-pressure we have found is owing to a depression of the heart, and to a similar condition of the medullary vaso-motor centre. The primary increase and final decrease in the respirations are due to stimulation and subsequent depression of the respiratory centres.

The fatal dose in the dog by the mouth is from 0.7 to 0.8 gram to the kilo of body-weight; by the jugular vein, from 0.5 to 0.6 gram to the kilo. The lethal dose in the frog is about 0.001 to 0.003 gram to the gram.

*Oxamide*.—This substance when given to dogs by the mouth in quantities as large as 5 grams to the kilo of body-weight is absolutely without any apparent action.

*Sulpho-carbamide*.—Twenty grams in divided doses were injected within twenty minutes into the jugular vein of a dog weighing 10 kilos, without producing other effects than a slight diminution of the pulse and a trifling increase in the respirations.

*Pyromucamide*.—This compound failed to produce any toxic symptoms in a dog weighing 7 kilos, after the intravenous injection of 30 grams in divided doses, within three-fourths of an hour. We are indebted to Prof. Henry B. Hill for the preparation employed.

#### *Anilides.*

*Formanilide*.—In the frog this substance causes a loss of voluntary movement, heightened reflexes, convulsions, and peculiar muscular tremblings. Sensibility and the reflexes are finally diminished, and general paralysis ensues. The muscles and nerves retain their irritability after death, but they are less excit-

able than normal. The spinal cord is first stimulated and then depressed. The convulsions are spinal.

When given to the dog by the mouth, or subcutaneously, there is noted general feebleness, languor, quickening of the respirations, an increase followed by a decrease of the pulse-rate, and sleep which deepens into stupor from which the animal can be aroused only with some effort. The reflexes are increased, a loud noise, or a blow upon the table, will bring on muscular movements of an unco-ordinated type. The patellar reflex is augmented; salivation is sometimes present; the temperature is lowered from  $1^{\circ}$  to  $2^{\circ}$  C., and slight convulsions are often observed. Should the dose be fatal, sensibility and the reflexes are diminished, the respirations are decreased in frequency, the heart's action becomes slower, the animal passes into a condition of collapse, and death results from a failure of respiration.

When the carotid artery is connected with the kymographion and the drug is given by the jugular vein in the dose of 0.06 gram to the kilo, the pulse is for a few moments increased and then diminished, and the arterial pressure is a little depressed. If the dose is as large as 0.1 gram to the kilo the pulse-rate is decreased and the pressure is slightly lowered. When this dose is several times repeated the slowing of the pulse gives place to an increase which exceeds the normal, but the pressure is more and more diminished. The respirations are quickened. Finally, as death approaches the heart-beats become slower and slower, although the pulse-curves are high and indicate that the viscus is far from being exhausted; the pressure is gradually lowered to zero; the respiratory movements become very slow, and death results from the cessation of respiration.

The primary decrease of the heart-beats we have found to be due to a stimulation of the cardio-inhibitory centres and ganglion; the frequent pulse, to their depression; and the slow pulse late in the poisoning, to a direct action on the heart. The fall of pressure is dependent almost solely upon a depression of the vaso-motor centres in the medulla oblongata, but the alterations in the heart-beats are also in part accountable. The changes in the respirations are due to a direct action on the respiratory centres, consequently the centres are first stimulated, then depressed. Death occurs from respiratory paralysis.

The fatal dose in the dog when given by the mouth is from 0.4

to 0.5 gram to the kilo of body-weight; when by the jugular vein, about 0.4 gram to the kilo. The lethal dose for the frog is about 0.0008 gram to the gram.

*Acetanilide*.—When this substance is given to dogs by the stomach, vomiting is so readily produced that it is only by repeated doses that a full toxic action can be studied. Doses of 0.5 gram to the kilo of body-weight cause salivation, vomiting, weakness, a lowering of the temperature from  $0.3^{\circ}$  to  $0.8^{\circ}$  C., an increase of the pulse, and a slight increase in the respirations. After repeated doses the weakness becomes marked, the animal is very sleepy, the temperature steadily falls, the pulse becomes weak and increased in frequency, tremors and convulsive movements occur, the blood is darkened, and the respirations are shallow and slower, and finally cease.

When injected directly into the circulation in doses of from 0.3 to 0.6 gram, the arterial pressure is lowered about 10 mm., and the pulse and respirations are increased in frequency. Repeated doses continue to lower the pressure; the pulse for a time is more and more increased, but after about the third dose, reaches its maximum and begins falling, steadily declining until death ensues. The respirations, however, show no tendency at any time during the progress of the poisoning to go below the normal until immediately before death, and are generally increased about two or three times the normal rate.

Doses as large as from 2 to 4 grams lower the pressure and pulse-rate and increase the respirations. After a dose of 2 grams the pressure will fall immediately about 20 mm., and gradually recover during the following fifteen minutes. The pulse is reduced about twenty per cent., and the respirations are doubled in frequency. Repeated doses of this size act more powerfully on the pressure than the first dose, but the effects on the pulse and respirations are not as marked. Even as much as 4 grams may be injected in a single dose without profoundly affecting the circulation.

After the isolation of the heart from the nerve-centres and the destruction of the vaso-motor centres in the medulla oblongata, the same changes in the pulse and blood-pressure ensue, so that these phenomena are of cardiac origin. The increase in the respirations is as well marked after section of the vagi as before, and is therefore due to an action directly on the respiratory cen-

tres. The blood is discolored, owing to the presence of methæmoglobin. Apart from a pronounced destructive action on the hæmoglobin and the consequent interference with functions of the red-blood corpuscles, acetanilide is certainly a feeble poison.

Death results from a failure of the respiratory centres.

We have not been able to determine the exact fatal dose in the dog when the drug is given by the stomach, but by the vein the lethal quantity in divided doses varies from 0.3 to 1.2 gram to the kilo of body-weight.

*Benzanilide.*—This substance may be given to dogs by the stomach in quantities as large as 5 grams to the kilo without inducing other obvious symptoms than a slight decrease in the animal's temperature.

When injected into the jugular vein in doses of 0.3 gram it temporarily slightly increases the arterial pressure, the pulse and the respirations, and lowers the temperature. A number of such doses may be given for a time, always causing a repetition of these effects, but finally the pressure and pulse show a downward tendency, while the number of respirations is increased. Although the actions on the circulation are far from being decided, there comes a time sooner or later when one of these doses will in a few seconds paralyse the heart. The effects on the circulation appear equally well after the isolation of the heart from the nerve-centres, and consequently are of cardiac origin. The alterations in the respirations are due to direct actions on the respiratory centres.

Benzanilide is in the form of fine micaceous crystals which are very insoluble, so that how far these effects are due to peculiar physiological properties of the drug *per se* is doubtful, but the absence of similar symptoms in animals after having been given such enormous doses by the stomach, certainly justifies the conclusion that the effects following its injection into the circulation are due to the mechanical actions of the undissolved particles clogging up the capillaries in the important centres.

(To be continued.)

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Contributions from the Laboratory of General Chemistry, University of Michigan.

## II. — THE CONSTITUTION OF ALIPHATIC KETONES, AND THE ACTION OF SODIUM ON ACETONE.

BY PAUL C. FREER.

Aliphatic ketones, in which the carbonyl group is attached to one or more negative groups of atoms, have been known for some time, and have since their discovery been a fruitful topic of discussion. It was in 1863 that Geuther<sup>1</sup> published his first paper on the action of sodium on acetic ether, by this means preparing sodium aceto-acetic ether,  $\text{CH}_3\text{CO.CHNa.COOC}_2\text{H}_5$ , which, when heated with methyl or ethyl iodide, yielded the corresponding alkylated derivatives of that substance. The discussion concerning the constitution of this interesting body has gradually drawn into the field of study the nature of other ketones and ketone-like substances which, similarly to aceto-acetic ether, give sodium derivatives on treatment with sodium or sodium ethylate.

The question as to the constitution of the ketones themselves has been intimately connected with that of their sodium derivatives, for chemists were divided in their opinion as regards the nature of these substances. Many, with Geuther as their chief representative, maintained that to possess acid properties these ketones must contain an hydroxyl group, just as other organic compounds do which act similarly under similar conditions, and that hence aceto-acetic ether possesses the formula  $\text{CH}_3\text{C(OH):CH.COOC}_2\text{H}_5$ , the hydrogen which is connected with oxygen being replaced by sodium in the formation of the metallic compounds. Opposed to this view was that of a large number who thought that more probably the constitution would be represented by the formula  $\text{CH}_3\text{CO.CH}_2\text{COOC}_2\text{H}_5$ , and consequently, that, in the sodium derivative, the metal is directly attached to carbon— $\text{CH}_3\text{CO.CHNa.COOC}_2\text{H}_5$ . The latter view was the one held by Frankland and Duppa,<sup>2</sup> who, simultaneously with Geuther, began a research on the action of sodium upon organic ethers. Geuther<sup>3</sup> assumed his formula to be the correct one because aceto-acetic ether had an acid nature (although it does not redden litmus and

<sup>1</sup> Jsb. Chem., 1863, 324.

<sup>2</sup> Ann. Chem. (Liebig) 138, 328; 219, 119.

<sup>3</sup> Jsb. Chem., 1865, 302.

its metallic compounds are decomposed by carbonic acid). His principal reasons for the theory were, however, based upon Wedel's production of dioxy-terephthalic ether (quinone-hydrodicarboxylic ether)<sup>1</sup> from dibromo-aceto-acetic ether. As dioxy-terephthalic acid readily yields hydroquinone on distillation, Geuther assumed the presence of two hydroxyl groups in the former, and accordingly, reasoning backward, this, to his mind, necessitated an acceptance of hydroxyl in dibromo-aceto-acetic ether, and therefore in aceto-acetic ether. Geuther advances the fact that dioxy-terephthalic ether readily yields a diacetyl derivative on being heated with acetyl chloride at 50°, as sufficient proof for the existence of two hydroxyl groups in dioxy-terephthalic ether, and the reverse should certainly be taken as an indication of the non-existence of such groups; yet, as I have experimentally proven, there is no reaction between aceto-acetic ether and acetyl chloride under conditions similar to those described by Wedel<sup>2</sup> for dioxy-terephthalic acid, while at higher temperatures acetyl chloride destroys aceto-acetic ether, forming ethyl chloride, carbon dioxide, acetone, acetic ether, and possibly carbaceto-acetic ether, although the analyses given by Wedel<sup>3</sup> are scarcely to be taken as agreeing with anything. Wedel assumes that, as hydrochloric acid must be formed from the acetyl chloride in order to produce these reactions, the hydrogen for the same is necessarily furnished by an hydroxyl group. Under the conditions of the experiment, however, nothing is easier to assume than that acetyl chloride acts as a dehydrating agent: the blackening of the oil referred to by Wedel seems to indicate this. The water so produced could then readily furnish hydrochloric acid. The experiments with acetyl chloride, then, not only fail to prove the presence of an hydroxyl group in aceto-acetic ether, but seem, indeed, to point toward its non-existence.

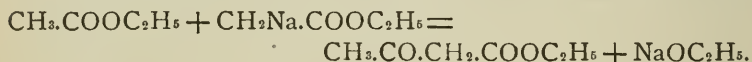
That dioxy-terephthalic ether contains two hydroxyl groups, no one will deny; but that fact seems to me to have no bearing upon the constitution of aceto-acetic ether itself. It is possible, however, that the introduction of negative groups in place of hydrogen in aceto-acetic ether, as is the case in the dibromo-aceto-acetic ether, would change the constitution of the substances from that of the true ketone to that of the unsaturated alcohol. Early in the history of aceto-acetic ether, Frankland and Duppa<sup>4</sup> discovered

<sup>1</sup> Ann. Chem. (Liebig) 219, 74.<sup>2</sup> Ibid. 85.<sup>3</sup> Ibid. 117.<sup>4</sup> Jsb. Chem., 1865, 304.

that the products of the action of methyl or ethyl iodide upon sodium aceto-acetic ether were decomposed—by heating with water, in a sealed tube, or by boiling with dilute acids—into alcohol, carbon dioxide and *substituted* ketones:



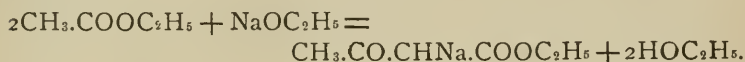
Frankland then formulated a reaction destined to once more open a wide field for discussion, explaining the formation of aceto-acetic ether from acetic ether and sodium; assuming the existence of a sodium acetic ether,  $\text{NaCH}_2.\text{COOC}_2\text{H}_5$ , which, when brought in contact with acetic ether, formed aceto-acetic ether, as follows:



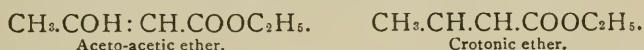
I need scarcely recall that this metallic derivative of acetic ether is as yet purely hypothetical. Lippman<sup>1</sup> strengthened Frankland and Duppa's view by making aceto-acetic ether from acetyl chloride, acetic ether and sodium. The view that in such a substance as acetic ether, sodium could replace hydrogen and attach itself to carbon, was believed in by the majority of chemists, although the sodium acetic ether had never been isolated. The statement is made that sodium does not attack perfectly dry acetic ether, free from alcohol. I dried some of the ether, first by allowing it to stand over night over granulated calcium chloride, which removed the greater part of the water and any alcohol which might have been present; I then boiled the ether for some time in a flask fitted with an inverted condenser, over phosphorus pentoxide, and after diluting with two or three volumes of equally dry ethyl ether, I added powdered sodium. A reaction at once set in, and continued until all of the sodium had disappeared. On filtering the solid formed, drying, and acidifying, there was nothing but aceto-acetic ether produced, showing that, even under circumstances which ordinarily produce these sodium compounds, the sodium acetic ether is converted into aceto-acetic ether. However, as the operation was performed with perfectly dry acetic ether, I cannot see how the acceptance of an intermediary sodium acetic ether is to be avoided. The impossibility of isolating it, however, might be taken as pointing toward a different structure for the methyl group in acetic ether, and for one of those supposed to exist in

<sup>1</sup> Jsb. Chem., 1868, 510.

acetone; and we might be strongly tempted to assume that the facility with which a hydrogen atom in the latter body is replaced by sodium indicates the existence of an hydroxyl group in the same. Geuther<sup>1</sup> believed that the assumption of the existence of sodium acetic ether was unnecessary, for sodium ethylate as well as sodium could produce aceto-acetic ether from acetic ether, as follows:

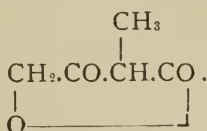


This view being at that time strengthened by the statements of Ladenburg,<sup>2</sup> Oppenheim and Precht,<sup>3</sup> and others, that sodium has very little, if any, action on perfectly-dry acetic ether, free from alcohol. Wislicenus<sup>4</sup> exhaustively reviewed the subject of the constitution of aceto-acetic ether and inclined toward the constitution  $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOC}_2\text{H}_5$ , chiefly because sodium aceto-acetic ether, when acted upon by ethyl or methyl iodide, yielded on saponification acetones substituted with alkyl radicles; and also because the substance is readily reduced to  $\beta$ -oxy-butyric acid by means of sodium-amalgam, while the corresponding unsaturated acid, crotonic acid, is not influenced by this reagent.



This latter point seems to me to be well taken; indeed, the behavior of so-called ketones toward reducing agents differs widely.

Some time ago I entered into the study of tetrinic acid, and, as a few of my experiments seem to me to have a bearing on the case, I will introduce them here. The constitution assigned to tetrinic acid by Michael<sup>5</sup> and Cornelius<sup>6</sup> is



The acid, or its sodium salt, on treatment with phenyl-hydrazine acetate, whether in aqueous or in alcoholic solution, yields a crystalline substance which crystallises in concentric prisms, sparingly soluble in hot water, soluble in hot dilute alcohol, from which it separates on cooling, the melting-point being  $191^\circ$ – $192^\circ$ . On

<sup>1</sup> Jsb. Chem., 1868, 511.

<sup>2</sup> Ber. d. chem. Ges. **3**, 325.

<sup>3</sup> Ibid. **9**, 320.

<sup>4</sup> Ann. Chem. (Liebig) **186**, 161.

<sup>5</sup> J. prakt. Chem. [2] **37**, 503.

<sup>6</sup> Ber. d. chem. Ges. **21**, 2607.

exposure to the atmosphere, as well as on recrystallisation from alcohol, this compound becomes pink, so that slight decomposition caused the nitrogen determination to be inaccurate.

Weight of substance, 0.2239 gram; formula,  $C_{11}H_{12}N_2O_2$ .  
*B*, 739.25 mm.; *t*, 20°; *N*, 24 cc.

	Calculated.	Found.
N	13.70	12.38

The figures, however, show that one formula-weight of phenylhydrazine has reacted with one of tetrinic acid. This is all that is at present necessary, for it shows that tetrinic acid, like other ketones, reacts with phenylhydrazine. I intend at some future time to investigate the substance more closely. Now, tetrinic acid, according to Demarcay, is not reduced by sodium-amalgam, and I took occasion to repeat his experiments, both in acid and in alkaline solution, in the heat and in the cold, and obtained, in the main, unchanged tetrinic acid, which was rendered impure by a small amount of a thick oil, the quantity of which in all cases was too small to render an investigation of its nature practicable. The result, then, shows that tetrinic acid, if at all reduced, is changed, only with the greatest difficulty, by nascent hydrogen, in which respect it resembles crotonic acid and other unsaturated compounds, and differs from aceto-acetic ether. Yet, were the two for-

mulæ as follows:  $CH_3.CO.CH_2.COOC_2H_5$  and  $CH_3.CO.CH.CO,$

there could be no reason why they should not act alike. If tetrinic acid be neutralised with sodium hydrate and evaporated to dryness, the sodium salt separates in reniform masses which are easily soluble in water, and which, on crystallising, contain three molecules of water of crystallisation. The salt is best obtained by dissolving tetrinate of sodium in a little water, adding four volumes of alcohol and then mixing the clear solution with an equal volume of ether, when the sodium salt crystallises in shiny plates. The salt, on standing over sulphuric acid *in vacuo*, becomes anhydrous, and can then be heated to 190° without any change—a characteristic distinguishing it from the sodium compound of aceto-acetic ether. The analysis of the dried salt resulted as follows:



0.3014 gram substance gave 0.1593 gram  $\text{Na}_2\text{SO}_4$ .

	Calculated.	Found.
Na	16.77	16.81

The dried salt was heated with an excess of ethyl iodide for eight hours at  $160^\circ$  in a sealed tube, when, with the exception of some darkening, no reaction seemed to have taken place. The salt remaining was acidified, heated with mercury to remove iodine, and repeatedly extracted with ether, when unchanged tetrinic acid separated upon evaporation. The sodium salt of tetrinic acid thus differs markedly from that of aceto-acetic ether, for that of the latter reacts with ethyl iodide quite readily. In order to prepare the ethyl ether, therefore, I was compelled to resort to the silver salt of the acid,<sup>1</sup> which, contrary to the statement of Demarcay, is tolerably soluble in water, separating therefrom in needles. This on treatment in the usual way with ethyl iodide gave the ether previously described by Cornelius.<sup>2</sup> It is an oil, insoluble in water, and in cold sodium hydrate; soluble in alcohol and ether; boiling at  $176^\circ$ – $178^\circ$  under 50 mm. pressure. On standing over night with potassium hydrate it dissolves completely, and on acidification yields crystals of an acid which has all the appearances and properties of tetrinic acid. The ether therefore differs from the products of the reaction of the alkyl iodides on the metal derivatives of aceto-acetic ether, for in this case the ethyl is evidently attached to oxygen, since it is saponified by alkalies. The analysis of the oil resulted as follows:

0.2574 gram substance gave 0.1665 gram  $\text{H}_2\text{O}$  and 0.5574 gram  $\text{CO}_2$ .

	Calculated for $\text{C}_7\text{H}_{10}\text{O}_3$ .	Found.
C	59.15	59.05
H	7.04	7.19

The crystalline substance resulting from the saponification of this ether gave on analysis the following results:

<sup>1</sup> Wedel, Ann. Chem. (Liebig) **219**, 106, prepared the ether of pentinic acid by saturating a solution of pentinic acid in alcohol with hydrochloric acid and allowing to stand eight days. The result was a very incomplete etherification. Cornelius follows out this method, with very poor results, his analyses showing that the ether was not as pure as the one I obtained from the silver salt. It is possible that my ether differs from that of Cornelius, for he describes his as a crystalline substance, melting at  $30^\circ$ . The boiling-points of the two are the same, and the analysis of my product proves its purity. Cornelius was unable to obtain tetrinic acid by saponifying this ether with alkalies, while mine readily hydrolyses, forming the salt of tetrinic acid.

<sup>2</sup> Moscheles and Cornelius: Ber. d. chem. Ges. **21**, 2603.



a lactone—an intra-molecular ether, where aceto-acetic ether,  $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ , is an ordinary inter-molecular one. Apparently the lactone grouping here is more negative than the carbethoxyl in aceto-acetic ether; the oxygen atoms, so to speak, surround the carbonyl group—provided we accept the existence of a carbonyl group in these substances. This would account for the increased stability of the salts, the ability of tetrinic acid to decompose carbonates of the alkalis, and also for the fact that tetrinic acid would more probably contain an hydroxyl group than a carbonyl group. Certain it is that tetrinic acid yields an acetyl derivative where aceto-acetic ether does not; and, just as certainly, aceto-acetic ether is readily reduced while tetrinic acid is not. At the time when Wislicenus wrote the paper referred to above, chemists saw no difficulty whatever in assuming that the sodium atom in the metallic derivatives of such bodies as we have under discussion, could be attached to a carbon atom, for at the time of the publication of the article referred to they became acquainted with the acid nature of the nitro-methanes, and unhesitatingly accepted this disposition of the sodium in the metallic compounds of the latter bodies, as, for example, in sodium nitro-methane,  $\text{O}_2\text{N}\cdot\text{C}\begin{smallmatrix} \text{H}_2 \\ \text{Na} \end{smallmatrix}$ . At the present time, however, many are coming to

agree with Michael,<sup>1</sup> who says: “Nach meiner Meinung existirt überhaupt kein Sauerstoffhaltiges Produkt, worin ein Metall direkt an Kohlenstoff gebunden ist, sondern es ist stets mit dem Sauerstoff gebunden.”

Of course, such a view necessitates the acceptance of a constitution for aceto-acetic ether differing from that of its sodium derivative, provided the deduction drawn from the behavior of tetrinic acid developed above be correct.

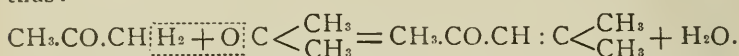
Wislicenus's paper, at the time of its publication, led to an almost universal acceptance of Frankland and Duppa's formula for aceto-acetic ether— $\text{CH}_3\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ . Sodium could then, despite its positive nature, be attached to carbon, while in closest proximity we have an oxygen atom, attached to carbon in such a way as to form an unsaturated compound, for the grouping  $\text{>C:O}$  must be considered as unsaturated. Some doubts were raised by a few chemists, notably by Claisen,<sup>2</sup> who published a research on the condensation-products of acetone,<sup>3</sup> and subse-

<sup>1</sup> J. prakt. Chem. [2] 3, 507.

<sup>2</sup> Ann. Chem. (Liebig) 218, 123.

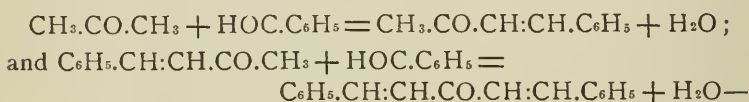
<sup>3</sup> Ibid. 180, 1.

quently one on the reactions which take place between aldehyde on the one hand, and acetone, aceto-acetic or malonic ether on the other. Claisen showed that when acetone is treated with hydrochloric acid, a condensation-product, mesityl oxide, is produced. In mesityl oxide the methyl group of one acetone molecule loses two hydrogen atoms in conjunction with an oxygen atom of another acetone molecule, producing water and the desired body, thus:

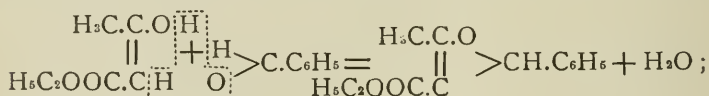


This reaction was subsequently extended so as to include all aldehydes, ketones and ketone-acids which contain a methyl- or methylene group in juxtaposition to the carbonyl- or carboxyl group. All of these bodies can part with the hydrogen of these groups, and this, with the oxygen of another ketone or aldehyde, will form water and leave a condensation-product. Claisen compared the action of aceto-acetic ether toward benzaldehyde with that of acetone.

If we ascribe the ketone formula to aceto-acetic ether, Claisen could see no reason why this substance should not behave exactly as does acetone, toward benzaldehyde. Acetone when condensed with benzaldehyde can form two products—



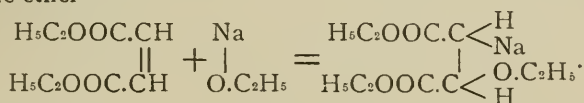
while aceto-acetic ether forms but one. For this reason Claisen concluded that the reaction took place as follows:



and that aceto-acetic ether is not a true ketone. The ethyl and methyl substituted-aceto-acetic ethers do not react with aldehyde at all unless under great provocation. These reactions would point to a difference in constitution between aceto-acetic ether and acetone, and in considering the subject should certainly be taken as evidence bearing on the case. However, it must be taken into consideration that Claisen's work only extended to the condensation of these aldehydes with aceto-acetic ether; he did not en-

deavor to prove that the substances so produced were not ketones, simply considering the difficulty of reaction with the methyl group as sufficient proof of their constitution. Moreover, he himself showed that<sup>1</sup> diethyl-aceto-acetic ether—where we undoubtedly have the ketone formula—reacts with aldehydes only with great difficulty. It seems to me that these condensation-reactions with aceto-acetic ether and similar substances are not sufficiently understood to enable us to draw conclusions therefrom, and, most certainly, will bear further investigation.

By reason of Claisen's work, and the investigations upon so-called tautomeric compounds, the whole subject was once more brought into prominence, and at that time Baeyer<sup>2</sup> took the field in behalf of the ketone constitution, laying great stress upon the work done by Purdie,<sup>3</sup> on the addition of sodium ethylate to fumaric ether—



In this reaction sodium is, undoubtedly, primarily attached to carbon, and, as the position of the sodium atom in sodium aceto-acetic ether and in similar ethers has been taken as a criterion of the constitution of these bodies—it being supposed that on substitution of the sodium by some radicle, this radicle would occupy the position vacated by the metal—the fact is of importance that a body can exist in which sodium is attached to carbon, even though oxygen be present in the compound. Baeyer acknowledges that in regard to aceto-acetic ether matters are complicated by the fact that, according to his theory of "Pseudo" forms, the atomic grouping  $-\text{CH}_2-\text{CO}-$  can change, under proper conditions, into  $-\text{CH}=\text{COH}-$  but calls attention to the fact that when acetyl chloride or acetic anhydride reacts with an organic compound containing the arrangement  $-\text{CH}=\text{CONa}-$ , an acetyl derivative having the acetyl connected directly with the oxygen, is always formed; while, when the same reagents are brought in contact with aceto-acetic ether, the acetyl group becomes attached to carbon. Hence he thinks we would be safe in saying that sodium aceto-acetic ether has a constitution which does not contain the group  $-\text{CH}=\text{CONa}-$ , but  $-\text{CO}-$

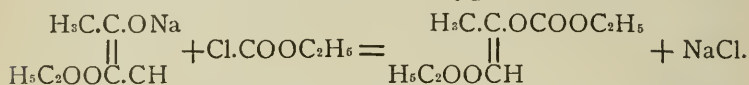
<sup>1</sup> Claisen and Mathews: *Ann. Chem.* (Liebig) **218**, 170.

<sup>2</sup> *Ber. d. chem. Ges.* **18**, 3454.

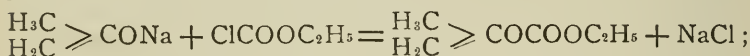
<sup>3</sup> *J. Chem. Soc.* **39**, 344; **47**, 855.



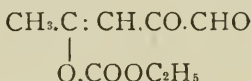
CHNa—. Michael<sup>1</sup> briefly mentions a reaction by which he obtains a neutral oil from the action of chlor-carbonic ether on sodium aceto-acetic ether, in which case he assumes that the group —COOC<sub>2</sub>H<sub>5</sub>— must be attached to oxygen, as follows:



Since then I have shown, as will be seen from the following paper, that the action of chlor-carbonic ether on sodium acetone produces a similar body, as follows:

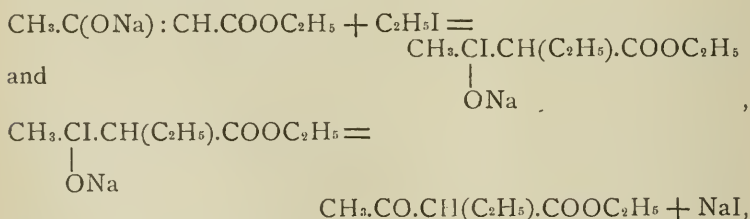


and a similar discovery, as yet unpublished *in extenso*, was made in Baeyer's laboratory by Zedel,<sup>2</sup> in trying the action of chlor-carbonic ether on sodium acetyl-acetone, the compound



being produced. We thus have three cases in which it seems to be proved that the sodium is not attached to the carbon but to the oxygen, in the sodium derivatives. This being the case, the formation of the ethyl, methyl, acetyl, and similar derivatives of aceto-acetic ether must be explained by assuming the formation of intermediary addition-products, for in all cases (saving that of chlor-carbonic ether) these radicles replacing sodium are undoubtedly attached to carbon.

The reactions, assuming the formation of intermediary addition-products, have been formulated by Michael<sup>3</sup> as follows:



with similar changes assumed for the other substitutions. From these reactions the constitution of the sodium derivatives of aceto-

<sup>1</sup> J. prakt. Chem. [2] 37, 474

<sup>2</sup> Alexander B. Smith: Inaugural Dissertation, Munich, 1889.

<sup>3</sup> J. prakt. Chem. [2] 37, 487 *et sub.*

acetic ether, acetone and similar ketones, seems undoubted—the sodium is attached to oxygen. What is the constitution of the free ketones? The answer is not by any means so easy, for here reactions seem to contradict one another much more. I have already called attention to the difference between tetrinic acid and aceto-acetic ether, which seems to argue in favor of the ketone-constitution of the latter; and to Claisen's researches, which seem to show the other formula to be the correct one. I will simply, therefore, in conclusion call attention to one or two reactions which seem to show a difference between the action of sodium aceto-acetic ether and aceto-acetic ether, and to point towards a difference in their constitution. Sodium ethylate, and even alcohol, can add itself to unsaturated compounds,<sup>1</sup> as Newbury and Chamot have shown. In a research undertaken by Michael and myself, the results of which are as yet unpublished, we show that sodium aceto-acetic ether can add itself to unsaturated ethers, exactly as sodium ethylate does. For instance, we have but to mix sodium aceto-acetic ether in alcoholic solution with cinnamic ether, and allow the whole to stand over night in the cold, when the sodium compound of the addition-product separates as a fine crystalline body.<sup>2</sup> To show the radical difference between sodium aceto-acetic ether and the free oil, I prepared the following experiments: I mixed aceto-acetic ether with cinnamic ether and heated in a metal bath until boiling, with no result. I then heated the mixture with zinc chloride in a sealed tube at 150° with no result; and finally with potassium carbonate at 180° for two days, when, besides the formation of a little dehydracetic acid, no result was observed. Aceto-acetic ether, therefore, does *not* add itself to unsaturated compounds in the manner of sodium aceto-acetic ether.

It occurred to me that acetone would give a sodium derivative similar to that of aceto-acetic ether, and with this end in view I began to experiment on the action of sodium on acetone—as was published in a short preliminary paper in this Journal<sup>3</sup>—and I will embrace this opportunity to give a more detailed account of this reaction. In order best to prepare acetone-sodium for use, small quantities of sodium (from one to two grams) should be finely powdered under boiling toluene, the oil carefully washed away

<sup>1</sup> This Journal 12, 519.

<sup>2</sup> The details of this research will appear shortly.

<sup>3</sup> This Journal 12, 355.

with dry ether, and the flask with the sodium and ether connected with an inverted condenser, a dropping-funnel, and an apparatus yielding pure and dry hydrogen. When all of the air has been expelled from the apparatus by means of the hydrogen, acetone, diluted with an equal volume of dry ether, is added through the dropping-funnel, when hydrogen is evolved and a white, flaky precipitate of acetone-sodium is formed. On standing this becomes dark red, but by quickly filtering, drying on a porous plate *in vacuo* over sulphuric acid and paraffin, I was enabled to obtain some analyses the numbers of which were published in the preliminary notice. It was necessary to prove, in the first place, that the gas evolved was hydrogen, and in the second, that the sodium derivative reproduced acetone on addition of dilute acids. In order to prove the first, a small flask was fitted with a dropping-funnel and gas delivery-tube, and then, after placing 0.05 gram sodium therein, the whole apparatus was filled with ligroine and the opening of the delivery-tube connected with a gas measuring-tube. Acetone was then added, and the reaction continued until all of the sodium had disappeared. The ligroine in the gas measuring-tube was then removed by washing with alcohol and water, when the remaining gas was found, in all of the experiments, to be only slightly less than that required for the displacement of one atom of hydrogen by one of sodium in acetone. The gas so obtained was analysed, and proved to be pure hydrogen. The first question is thus settled—sodium reacts with acetone, generating hydrogen. One gram of powdered sodium was placed under anhydrous ether, acetone was added as described previously, the sodium compound formed was quickly filtered, dried on a porous plate and added to water. The slightly-yellow solution was acidified with dilute hydrochloric acid, and extracted repeatedly with ether; the ethereal solution was dried over calcium chloride and the ether distilled, when no residue remained. There is therefore no sodium compound of a condensation-product of acetone contained in the substance. The operation was repeated with one gram of sodium, the sodium compound formed acidified with dilute hydrochloric acid and the solution tested for acetone, without shaking with ether. The tests employed for acetone were (1) the iodoform test, (2) the test with precipitated oxide of mercury. Both of these showed large quantities of acetone to be present. The second question also is therefore answered.

Acetone-sodium regenerates acetone on the addition of acids. The mother-liquors from a number of operations by which acetone-sodium had been prepared, were united, washed with water, dried over calcium chloride and the ether distilled. A small quantity of a dark-colored oil remains, which on fractioning had approximately the odor and boiling-point of mesityl oxide, the quantity being too small, even from a large number of operations, to have its constitution definitely settled, nor, indeed, is that necessary, as the acetone-sodium is the only object of interest. The fact remains that a certain amount of a higher-boiling condensation-product is formed at each operation in the preparation of acetone-sodium. The latter is a white, amorphous substance, which, when exposed to the atmosphere, rapidly decomposes and turns red; it is therefore, as would be expected, considerably less stable than is sodium aceto-acetic ether. When perfectly dry it can be kept apparently unchanged for some time.

The problem which presented itself now was to determine, if possible, the position of the sodium atom in this derivative, and with this end in view Mr. Higley and I studied the action of chlor-carbonic ether on acetone-sodium, the results of which investigation are contained in the following paper. The same questions, of course, arise with regard to the constitution of acetone, as did in regard to that of aceto-acetic ether; yet we would be slow to accept such an unfamiliar formula as  $\text{CH}_3\text{.COH:CH}_2$  for the former substance. Undoubtedly acetone has some of the characteristics of an unsaturated compound, as, for instance, when treated with gaseous hydrochloric acid, the latter is rapidly and completely absorbed; and when acetone and sulphuric acid are brought together, a violent reaction results, with the formation of a compound apparently similar to ethyl- and methyl-sulphuric acids.<sup>1</sup> I hope by an investigation of these substances to throw some further light upon the constitution of acetone. For the present, I believe that we must, in consideration of the difference in behavior of the free ketones from unsaturated compounds, conclude that the old formula containing the carbonyl group should be assigned to them; and that the sodium derivatives prepared from these substances contain the group  $\text{—CONa=C—}$ . In the reactions which I have cited, it will have been observed, however, that a number of changes which the ketones undergo can best be

<sup>1</sup> Kane: *Ann. der Phys. Pogg.* **24**, 479.

explained by the assumption that they contain the grouping  $\text{—COH=C—}$ . This chameleon-like behavior of these substances points toward a great instability of either atomic grouping, so that our future investigations will, possibly, show us that these bodies can assume either of the constitutions assigned to them. The sodium derivatives, however, always contain the grouping given above.

In this paper I have not taken into consideration the question of tautomerism in the aromatic series or its derivatives, which has been of late so beautifully elucidated by Nef. I am inclined to think that the considerable differences which exist, even between the di-, tetra-, and hexahydro benzene derivatives and those of the fatty series, often render conclusions drawn in the one inapplicable in the other.

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### III.—THE ACTION OF CHLOR-CARBONIC ETHER ON ACETONE-SODIUM.

BY PAUL C. FREER AND GEORGE O. HIGLEY.

In order to prove the nature of the sodium derivative, and also with a view to ascertaining the position of the sodium atom in the acetone radicle, we performed the experiments, the details of which are given below.—

Finely-powdered sodium is placed in an Erlenmeyer flask and covered with anhydrous ether; the flask is then connected with an inverted condenser, dropping-funnel, and an apparatus yielding pure hydrogen, and, after replacing the air with hydrogen, acetone is slowly added, until all of the sodium has been changed to acetone-sodium. Chlor-carbonic ether is then gradually dropped in, when a most violent reaction results, the ether boiling and the acetone-sodium becoming dark-colored. When the amount of chlor-carbonic ether calculated for the sodium has been added, the whole is allowed to stand for an hour or two, when the reaction with the chlor-carbonic ether will have been entirely finished, chloride of sodium having separated as a white precipitate at the bottom of the flask. It is best to perform this operation with small quantities of sodium, acetone and chlor-carbonic ether—say, 1 gram of sodium, an excess of acetone, and 4.7 grams of chlor-carbonic ether—and to unite the results of about ten reactions in



which these quantities have been used, before attempting to isolate the bodies formed. When a sufficient amount has been prepared, water is added to dissolve the sodium chloride; the ether is separated and washed several times with water, dried over calcium chloride and then evaporated, when a yellow oil remains, of which the major portion, on fractional distillation, boiled between  $125^{\circ}$  and  $135^{\circ}$ , while a minor part passed over as the temperature rose to  $250^{\circ}$ . The high boiling portion contains an oil boiling between  $112^{\circ}$ – $112\frac{1}{2}^{\circ}$ , at 30 mm. pressure, and which will be the subject of a future investigation. The low boiling portion was fractioned several times, after which it distilled at  $128^{\circ}$ – $129^{\circ}$ .

The first analysis resulted as follows:

I. 0.1089 gram substance gave 0.1021 gram  $H_2O$  and 0.2275 gram  $CO_2$ .

II. 0.1685 gram substance gave 0.1462 gram  $H_2O$  and 0.3518 gram  $CO_2$ .

	Calculated for $C_6H_{10}O_3$ .	Found.	
		I.	II.
C	55.40	56.96	56.96
H	7.60	10.20	9.64

Evidently, provided an isomer of aceto-acetic ether had been formed, the oil contained some substance which increased the amount of carbon and hydrogen, and mesityl oxide, with a percentage of 73.46 for the carbon would change the numbers found on analysis, even though present in but small quantities, quite markedly; while its removal by distillation would be impossible, as its boiling-point is  $130^{\circ}$ . As a consequence of this theory, the oil was treated with phenyl-hydrazine and allowed to stand for a little while, a slight warming taking place on the addition of this reagent. The whole was then driven over with steam, the oil collected in the receiver, shaken out with ether, and then dried over calcium chloride, and the ether evaporated, when the residual oil, on fractioning until apparently pure, was analysed.

I. 0.1371 gram substance gave 0.2775 gram  $CO_2$  and 0.1149 gram  $H_2O$ .

II. 0.1226 gram substance gave 0.2499 gram  $CO_2$  and 0.1004 gram  $H_2O$ .

	Calculated for $C_6H_{10}O_3$ .	Found.	
		I.	II.
C	55.40	55.10	55.73
H	7.60	9.10	9.10

In each case the percentage of hydrogen found has been too high, so that the purity of the substance must be doubted, yet in all probability the impurity boils at exactly the same temperature as does the oil itself, so that it is not to be removed by fractioning. We hope, during next year, when our supply of chlor-carbonic ether will be replenished, to repeat the formation of this body, with the hope of securing more accurate hydrogen determinations. The constitution of the body is, however, abundantly proved by the following experiments.

A determination of the vapor-density of the oil, according to the Victor-Meyer method, gave the following results:

Substance.	<i>T.</i>	<i>V.</i>	<i>B.</i>	<i>D.</i>	
				Calculated.	Found.
I. 0.1359 gram.	30°	29.6 cc.	733 mm.	4.50	4.27
II. 0.2040	29	50	733	4.50	4.44

The density of 4.44 calls for a molecular weight of 128.18, while that of aceto-acetic ether is 130, showing conclusively that here we have to deal with a substance of equal molecular weight.

The product of the action of chlor-carbonic ether on sodium-acetone is a colorless oil, insoluble in water, soluble in alcohol and ether in any proportion, possessing a pleasant, fruity odor, and boiling at 128°–129°. It does not react with phenyl-hydrazine, nor does its alcoholic solution give any color-reaction with ferric chloride. On heating in a sealed tube with dilute hydrochloric acid, it is decomposed into carbon dioxide, alcohol, and acetone. There remains a slight odor as of a hydrocarbon, which may possibly indicate the impurity which rendered the analyses inaccurate.

In order more definitely to study the products formed, this decomposition was performed quantitatively. For this purpose an Erlenmeyer flask was fitted with a double-bored stopper, into one of the openings of which was placed a tube connecting with a train of gas wash-bottles containing caustic potash; into the other was placed an inverted condenser, connected by means of a long double-bent tube, with a train of sulphuric-acid wash-bottles, and with the ordinary potash combustion-bulbs; a slow stream of air could be passed through the apparatus by means of an aspirator. A weighed quantity of substance was now placed in the flask with 250 cc. of dilute hydrochloric acid (1 to 20); air was passed through until all carbon dioxide had been expelled from the apparatus; the potash-bulbs were attached, and the liquid then

heated to boiling. In this manner all of the carbon dioxide given off could be collected in the potash-bulbs, while any accidental diffusion backward toward the caustic-potash train was prevented by placing a Bunsen valve at the end of the tube connecting that portion of the apparatus with the Erlenmeyer flask. The determination was made several times, but as the results ran very close together, I will enter but one of them here.

Substance used, 0.4992 gram.

CO<sub>2</sub> found at the end of 9 hours, 0.1152 gram.

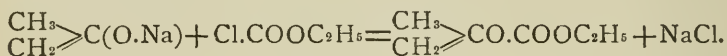
15	0.1324
24	0.1472
33	0.1576
42	0.1618
51	0.1665
59	0.1666

	Calculated.	Found.
CO <sub>2</sub>	33.84	33.38

This reaction is interesting in several ways, showing as it does the character of such saponifications. In the first nine hours, about 70 per cent. of the ether is decomposed; in fifteen hours, about 79 per cent.; in twenty hours, about 88 per cent.; the reaction continuing with diminishing velocity until at the expiration of fifty-one hours it is complete, the potash-bulbs gaining but 0.0001 gram in the following eight hours. This reaction shows conclusively that the product of the action of chlor-carbonic ether on acetone is saponified by boiling with dilute hydrochloric acid, yielding carbon dioxide. In order to determine the other substances formed, the hydrochloric acid remaining after saponification was partially distilled on a sand-bath, the distillates from several operations united and redistilled, until a moderately concentrated solution of the supposed acetone and alcohol was obtained. A portion of this was treated with acetic acid and sulphuric acid, boiled for a short time in a flask fitted with an inverted condenser, and then distilled, when acetic ether passed over, showing conclusively that alcohol as well as carbon dioxide had been produced. Lastly, the remaining portion was tested for acetone according to two methods: (1) by means of the test with precipitated oxide of mercury; and (2) by means of phenyl-hydrazine acetate; both of which showed acetone to be present. The oil therefore decomposes into carbon dioxide, alcohol, and acetone.

These results may be summed up as follows:

The oil produced by the action of chlor-carbonic ether on acetone-sodium gives figures on analysis, and possesses a vapor-density, which show it to be an isomer of aceto-acetic ether. It does not react with phenyl-hydrazine, nor does it give a color-reaction with ferric chloride, showing a marked difference in properties from aceto-acetic ether. It is decomposed into carbon dioxide, acetone, and alcohol on boiling with dilute acids. All of these reactions seem to show that we have to deal with a body formed as follows:



The body forms addition-products with bromine, but slowly, but when placed in the sunlight *substitution* takes place rapidly, all of the products formed being of an oily nature, which rendered purification impossible. This indifference toward bromine might be taken as arguing against the formula given above, but then we must consider that, not unfrequently, unsaturated organic compounds, where their nature is extremely negative, do not take up bromine at all—as, for example, in the case of the dicarbon-tetracarbonic ether  $\begin{array}{c} \text{COOC}_2\text{H}_5 \\ \diagup \\ \text{COOC}_2\text{H}_5 \end{array} > \text{C} = \text{C} < \begin{array}{c} \text{COOC}_2\text{H}_5 \\ \diagdown \\ \text{COOC}_2\text{H}_5 \end{array}$  of Conrad and Guthzeit.<sup>1</sup>

Another point to which, in fairness, attention should be called is the low boiling-point of the substance, 128°–129°. This should not, however, be taken as counterbalancing the definite proofs of the constitution of the substance given above, as, in the first place, but two or three substances of this class are known, and, in the second, isomers often exhibit very varying boiling-points. There seems indeed no formula, other than the one assigned above, possible for an isomer of aceto-acetic ether synthesised as has been the substance prepared by us. There seems to be no doubt, therefore, that in the case of acetone-sodium the metal is attached to oxygen.

We intend to continue the investigation of this most interesting substance.

<sup>1</sup>Ann. Chem. (Liebig) 214, 76.

## THE PROTEIDS OR ALBUMINOIDS OF THE OAT-KERNEL.<sup>1</sup>

BY THOMAS B. OSBORNE.

### I.—HISTORICAL.

The proteids contained in or derived from the oat-grain have been specially studied by J. P. Norton, Baron von Bibra and Dr. W. Kreusler. Norton<sup>2</sup> recognised three proteids, *viz.* 1. *Albumin*—0.5–2.17 per cent.—which was taken up from the “epidermis” (after starch had been mechanically removed by elutriation with slightly ammoniacal water), by boiling with acetic acid, and was precipitated by neutralising the solution. 2. *Casein* (or *avenine*, as Johnston, in whose laboratory the work was done, named it)—15.76–17.72 per cent.—which was dissolved in the slightly ammoniacal water used in separating starch, and thrown down by acetic acid. 3. *Glutin*—1.33–2.47 per cent.—extracted by alcohol and separated from oil by means of ether, and from sugar by water.

Von Bibra<sup>3</sup> found that no coherent gluten could be got from oat-flour by kneading in water. He recognised *Albumin*—1.24–1.52 per cent.—precipitated by boiling the cold-water-extract of the ground oats; *Casein*—0.15–0.17 per cent.—the body separating from the hot alcohol-extract on cooling; *Plant-gelatin* (Dumas’ *glutin*, Taddei’s *gliadin*)—3.00–3.25 per cent.—the substance soluble both in hot and cold alcohol; and *Nitrogenous substance insoluble in water and alcohol*—11.38–14.85 per cent.

Kreusler<sup>4</sup> found *Oat-Gliadin* soluble in weak alcohol and *Oat-Legumin* soluble in very dilute alkali.

Since the date of Kreusler’s work, 1869; our knowledge of proteid bodies and of the methods for their investigation has been considerably extended. This advance has been chiefly in the study of the animal proteids, but little real progress having been made in our knowledge of the vegetable albuminoids. The following research was undertaken with a view to applying the newer

<sup>1</sup> An abstract of this paper was read by the author before the National Academy of Sciences, in Boston, November 13th, 1890.

<sup>2</sup> Am. J. Sci. [2] 3, 330 (1845); 5, 22 (1848).

<sup>3</sup> Die Getreidearten und das Brod (Nürnberg, 1860).

<sup>4</sup> J. prakt. Chem. 107, 17.



methods of study to the plant-proteids that have agricultural importance.

## II.—OAT-PROTEIDS EXTRACTED BY WEAK ALCOHOL.

### (a) *Kreusler's Work.*

The oat-proteid soluble in weak alcohol was first examined, and, as results differing from *Kreusler's* were obtained, it will be well to give here a brief summary of his work.

*Kreusler* found that, on extracting ground oats with alcohol of 80 per cent. and concentrating the extract to one third of its volume, a considerable amount of substance separated which, after subsiding from the solution, became a tough, transparent mass of amber-yellow color. The solution decanted from this substance and further concentrated yielded a second deposit. The liquid poured from this second deposit yielded, on still further concentration, a third. The three sediments were united and dissolved in 80 per cent. alcohol at a gentle heat. On cooling, the greater part of the substance precipitated. After decanting the liquid, this precipitate was treated with absolute alcohol, which caused it to gather on the walls of the vessel as a tenacious mass. After treating with ether and again with absolute alcohol, it was dried over sulphuric acid. This *Kreusler* designated "A."

By concentrating the solution decanted from A, on cooling, he obtained a second precipitate "B." The filtrate from B by similar treatment yielded a third precipitate "C."

These three precipitates showed the same behavior with various reagents and appeared to differ only in their degree of purity. The reactions agreed with those of gliadin from wheat, which, according to *Ritthausen*, contains 18 per cent. of nitrogen.

*Kreusler* found that :

A	contained	16.22	per cent.	of nitrogen.
B	"	16.21	"	" " "
C	"	15.36	"	" " "

These three preparations were united, dissolved in dilute acetic acid and fractionally precipitated by dilute potash. Thus were obtained three precipitates :

I	with	16.00	per cent.	of nitrogen.
II	"	16.51	"	" "
III	was too small in amount for analysis.			

By this treatment the substance was separated into two portions of different nitrogen-content.

Kreusler in the next place prepared a new extract with alcohol of 80 per cent. from five pounds of ground oats, concentrated the solution until nearly all the alcohol was removed, and on cooling and treating the precipitate with ether and absolute alcohol and drying over sulphuric acid, obtained thirty grams of substance having properties like the former preparations, but not wholly soluble in acetic acid. This precipitate contained 15.36 per cent. of nitrogen. When it was heated with acetic acid, a residue was left, having 14.81 per cent. of nitrogen. The acetic-acid solution by three partial precipitations with dilute potash, gave, as before, precipitates I, II and III—the third being too little for analysis. The composition was :

	I.	II.
Carbon	...	53.41
Hydrogen	...	7.15
Nitrogen	16.99	17.14

This treatment, however, had failed to yield a product having as much nitrogen as Ritthausen's gliadin.

I and II were, therefore, united and dissolved in 60-per cent. alcohol at a gentle heat. The solution was brownish yellow, and on cooling a part of the substance precipitated. The filtrate from this precipitate gave a second precipitate when treated with absolute alcohol. These precipitates were united and called A. The alcoholic filtrate contained a considerable amount of substance which was separated by concentration and gradual precipitation with absolute alcohol. This precipitate was marked B and resembled A in appearance. They contained :

	A.	B.
Carbon	...	52.64
Hydrogen	...	7.66
Nitrogen	17.71	16.70

Since the substance was precipitated in the presence of a considerable amount of acetic acid and might be thought to retain some of the latter, the just-described process was repeated with A, and potash added to perfect neutralisation. The precipitate thus obtained was slightly washed with water, and after dissolving in 60-per cent. alcohol was precipitated with absolute alcohol. B

was dissolved directly in weak, and precipitated by absolute alcohol. These products then had the following composition :

	A.	B.
Carbon	52.94	53.12
Hydrogen	7.71	8.15
Nitrogen	{ 17.28 17.30	17.20

These preparations were next united and dissolved by heating in 60-per cent. alcohol; a varnish-like mass deposited on cooling. This process was repeated several times, and the substance was finally dried with absolute alcohol. It had the following composition, as found in analyses I and II :

	I.	II.	Gliadin.	
			Oats (Kreusler).	Wheat (Ritthausen).
Carbon	52.94	52.59	52.59	52.60
Hydrogen	7.58	7.65	7.65	7.00
Nitrogen	17.71	...	17.71	18.06
Sulphur	1.71	1.61	1.66	.85
Oxygen	20.06	...	20.39	21.49
	<hr/> 100.00		<hr/> 100.00	<hr/> 100.00

The alcoholic solution after concentrating gave on cooling a preparation with 17.2 per cent. nitrogen. Kreusler rejected the highest carbon-determination (obtained without the use of lead dioxide) as probably erroneous, and wrote his analysis of *oat-gliadin* beside Ritthausen's analysis of *wheat-gliadin*, as quoted above. Kreusler concludes that oat-gliadin is essentially different from wheat-gliadin, and compares at length the behavior of the two towards reagents. The one point of difference he mentions is that the oat-gliadin dissolves in concentrated hydrochloric acid to a scarcely-colored liquid, while wheat-gliadin gives a blue solution.

It is evident from Kreusler's paper that he expected to find the oat-proteid soluble in alcohol to have the same composition as wheat-gliadin. He finally accepted, as pure, a preparation having 17.71 per cent. of nitrogen, according to a single determination.

It is to be noticed on reviewing his analyses that the treatment to which Kreusler submitted his preparations, while on the whole tending to raise the nitrogen-content, sometimes appears to have had the opposite effect, and the conclusion is not improbable that

the fluctuations in the percentage of nitrogen found by him are partly attributable to the then unknown errors involved in the soda-lime method of analysis—errors which Ritthausen<sup>1</sup> and U. Kreusler<sup>2</sup> in later years fully appreciated and made the subject of special investigation.

### III.—OAT-PROTEIDS EXTRACTED BY WEAK ALCOHOL.

#### (b) *The Writer's Work.*

##### 1. *Direct Extraction with Alcohol,—Preparations 1-8.*

As Ritthausen had separated the gliadin, mucedin and fibrin found by him in wheat-gluten, from alcoholic solution by fractional precipitations, the writer judged that if more than one proteid were extracted from oats by alcohol, this fact would be shown by differences in behavior and composition of various fractions of the alcoholic extract. Accordingly four kilos of freshly-ground oats were heated on the water-bath with ten liters of alcohol of 0.915 sp. gr. After boiling for half an hour the extract was strained through cloth, the residue pressed out and the extraction repeated. The extracts were united, allowed to stand over night, decanted from sediment and filtered clear. This solution was concentrated to one-third by distillation. After standing for twenty hours at the temperature of the room, the residue deposited a bulky, yellowish precipitate. About four-fifths of the solution was carefully decanted from this precipitate. The remaining one-fifth could not be filtered until a large amount of strong alcohol had been added, which caused the precipitate to separate. After filtering, the precipitate was treated with absolute alcohol, next with ether, and after removing the ether, with absolute alcohol again, and dried over sulphuric acid. This preparation, "1," then weighed 15.5 grams and, dried at 110° C., contained 13.92 per cent. of nitrogen. The liquid decanted from 1 was still further concentrated to about one-third of its volume and cooled. The precipitate which formed "2" was treated with absolute alcohol and ether, and, after drying over sulphuric acid, weighed 10.30 grams. Dried at 110° C., it contained 12.36 per cent. of nitrogen. The filtrate from 2 was concentrated to a thick syrup. On cooling, a deposit formed on the bottom of the dish. The syrup was

<sup>1</sup> Pflüger's Archiv 18, 236 (1878).

<sup>2</sup> Landw. Vs-St. 24, 37 (1880); ibid. 31, 248 (1885).

poured off and this deposit treated successively with strong alcohol, absolute alcohol, ether, and finally with absolute alcohol again. After drying over sulphuric acid, this precipitate, "3," weighed 6.82 grams, and contained, when dried at 110° C., 10.37 per cent. of nitrogen.

The alcoholic liquids obtained by washing preparations 1, 2 and 3 were found to have dissolved a large amount of proteid; they were, therefore, united and concentrated on the water-bath to small volume, and cooled. The abundant deposit was washed with absolute alcohol, ether, absolute alcohol again, and dried over sulphuric acid. The 14.62 grams thus obtained, "4," when dried at 110° C., contained 16.27 per cent. of nitrogen. The filtrate from 4 was still further concentrated, and after cooling and adding a large amount of alcohol, gave a precipitate, "5," which, when treated as the others, weighed 4.21 grams and contained 6 per cent. of nitrogen. The filtrate from 5 was highly concentrated and treated with absolute alcohol. The precipitate thus thrown down, "6," after treating with absolute alcohol, ether, absolute alcohol again, and drying over sulphuric acid, weighed 17.78 grams and contained 8.61 per cent. of nitrogen.

To sum up: From the alcoholic extract, by concentrating and cooling three times, there resulted three preparations, *viz.*:

1, of 15.5 grams, containing 13.92 per cent. of nitrogen.

2, of 10.30 " " 12.36 " "

3, of 6.82 " " 10.37 " "

From the alcoholic washings of 1, 2 and 3 by concentration and cooling was obtained preparation

4, of 14.62 grams, containing 16.27 per cent. of nitrogen.

And by further concentration and addition of much strong alcohol,

5, of 4.21 grams, containing 6 per cent. of nitrogen.

6, of 17.78 " " 8.61 " "

The principal impurity recognised in these preparations was sugar, which was abundant in 5 and 6.

These six preparations were examined separately.

1 was warmed with alcohol of 75 per cent., but was only partly soluble, and owing to its slimy nature, could not be filtered. Three volumes of strong alcohol were added, making the solvent equivalent to 2 liters of about 88-per cent. alcohol. After heating to boiling and cooling, a little substance separated, which was filtered



out, together with the undissolved portion. This precipitate and residue, "1A," after treatment with absolute alcohol, ether, etc., as before described, weighed 3.68 grams and contained 14.57 per cent. of nitrogen.

The filtrate from 1A, concentrated to one-third and cooled, deposited but little substance. Addition of an equal volume of water produced a precipitate. The liquid was poured off and the deposit treated with a large amount of absolute alcohol. The residue, "1B," after drying, weighed 3.05 grams, and contained 15.39 per cent. of nitrogen. Water was added to the filtrate from 1B, but only a trifling precipitate resulted. The aqueous solution was then boiled, the coagulum filtered off, washed with absolute alcohol and dried over sulphuric acid. This preparation, "1C," weighed 2.45 grams and contained as follows:

COAGULATED PROTEID.—*Directly extracted from Ground Oats by Weak Alcohol—1C.*

Carbon	52.66
Hydrogen	6.89
Nitrogen	16.32
Sulphur	}
Oxygen	
Ash	24.13
	<hr/>
	100.00

*Carbon and hydrogen.*—0.3120 gram, dried at 110° C., gave 0.6025 gram CO<sub>2</sub> = 52.66 per cent. C, and 0.1934 gram H<sub>2</sub>O = 6.89 per cent. H.

*Nitrogen* (by Kjeldahl method).—0.5624 gram, dried at 110° C., gave ammonia = 10.75 cc. HCl (1 cc. HCl = 0.00854 gram N) = 16.32 per cent.

*Ash* could not be determined for want of material.

Nothing more could be obtained out of the filtrate from 1C.

2 and 3 were united and treated with 400 cc. of boiling alcohol of 0.9 sp. gr. A part dissolved to a deep-red solution. The residue was extracted again with hot dilute alcohol and treated in the same manner as the other preparations. Thus was obtained 9.05 grams of substance "2 and 3A" containing 15.47 per cent. of nitrogen.

This preparation was again treated first with hot water and then with hot alcohol of 0.9 sp. gr., but only a little dissolved and the nitrogen-content was unchanged.

The alcoholic filtrate from **2** and **3A** was further examined, but only 2.3 grams of substance with 7.66 per cent. of nitrogen, were obtained. The long heating in very weak alcohol to which preparations **2** and **3** had been subjected, had rendered a large share of the proteid insoluble, and it was therefore lost for further purification.

**4** was treated with 500 cc. of alcohol of 0.9 sp. gr., in which a part was insoluble, "**4A**." This was washed with alcohol and ether, dehydrated with absolute alcohol, and, after drying over sulphuric acid, weighed 8.9 grams. Its analysis follows:

COAGULATED PROTEID.—*Directly extracted from Ground Oats by Weak Alcohol—4A.*

Carbon	53.09
Hydrogen	6.96
Nitrogen	16.56
Sulphur }	23.39
Oxygen }	
	100.00
Ash	.35

*Ash*.—0.5069 gram air-dried (= 0.4555 dried at 110° C.) gave 0.0016 gram ash = .35 per cent.

*Carbon and hydrogen*.—0.4354 gram, dried at 110° C., gave 0.8445 gram CO<sub>2</sub> = 52.90 per cent. C, and 0.2716 gram H<sub>2</sub>O = 6.91 per cent. H.

*Nitrogen* (by Dumas' method).—0.5425 gram, dried at 110° C., gave 76.12 cc. gas at 9° C. (barometer 756.3 mm. at 9° C.) = 16.76 per cent., less correction of .20 = 16.56 per cent. N.

The alcoholic filtrate from **4A** was concentrated to small volume, but as a slimy precipitate appeared, which could not be filtered, the solution was mixed with water. This did not cause the substance to separate in a manageable form, so the liquid was boiled, and after cooling the substance deposited as a gelatinous lump. After filtering, the deposit, "**4B**," was treated with absolute alcohol and with ether and dried over sulphuric acid. It weighed 2.6 grams. Its analysis is subjoined:

COAGULATED PROTEID.—*Directly extracted from Ground Oats by Weak Alcohol—4B.*

	I.	II.
Carbon	53.12	...
Hydrogen	6.91	...
Nitrogen	16.52	16.39
Sulphur	23.45	...
Oxygen		
Ash		
	<hr/>	
	100.00	

*Ash.*—Very little. Not determined for want of substance.

*Carbon and hydrogen.*—0.3445 gram, dried at 110° C., gave 0.6700 gram CO<sub>2</sub> = 53.12 per cent. C, and 0.2143 gram H<sub>2</sub>O = 6.91 per cent. H.

*Nitrogen, I* (by Dumas' method).—0.2693 gram, dried at 110° C., gave 37.93 cc. gas at 8° C., less correction of .7 cc. (barometer 756.3 mm. at 9° C.) = 16.52 per cent. N.

*Nitrogen, II* (by Kjeldahl method).—0.2693 gram substance, dried at 110° C., gave ammonia = 9.68 cc. HCl (1 cc. HCl = 0.00854 gram N) = 16.39 per cent.

The filtrate from 4B was evaporated to dryness and yielded one gram of substance containing 7.5 per cent. of nitrogen.

6 evidently contained a large amount of sugar. It was first treated repeatedly with water, in which it formed a pasty lump. This was dehydrated with absolute alcohol, and when dried over sulphuric acid weighed 7.63 grams and contained 14.61 per cent. of nitrogen = "6A."

6A was then treated with 100 cc. of water, with which it formed a stringy lump which, after having been thoroughly kneaded under water, assumed a semi-liquid condition and could not be separated from the solution either by boiling or freezing. The solution after concentrating on the water-bath to about 30 cc. was poured into 300 cc. of absolute alcohol. This threw down a curdy white precipitate which, after treating with absolute alcohol and drying over sulphuric acid, weighed 6 grams, and contained 15.67 per cent. of nitrogen when dried at 110° C. = "6A1."

6A1 was treated with 500 cc. of alcohol of 0.9 sp. gr. But little dissolved and the solution was too slimy to filter. The

whole was then concentrated to one-third and cooled, but no separation took place which would allow of filtering or decanting the solution. The solution was, therefore, diluted with water and boiled. After cooling, a curdy precipitate settled out, leaving a turbid liquid. This liquid was decanted and poured into a large amount of absolute alcohol. On standing, a precipitate separated which, when treated with absolute alcohol and dried over sulphuric acid, weighed 0.455 gram and contained, when dried at  $110^{\circ}\text{C}.$ , 16.40 per cent. of nitrogen = "6A2."

There was thus obtained of the proteid soluble in alcohol a large number of fractional precipitations with different nitrogen-content. It will be noticed, however, that five of these preparations have from 16.27 to 16.56 per cent. of nitrogen. No preparations were obtained having a higher percentage of nitrogen, and none of the other preparations approximate to a constant nitrogen-content.

4 had 16.27 per cent. of nitrogen. When this was separated into two parts, one soluble in dilute alcohol—4B—and the other insoluble—4A—the two parts were found to contain the same proportion of nitrogen, and exactly agreed in content of carbon and hydrogen. This is what might be expected of a pure proteid, for some of these bodies become insoluble without change of composition, so far as can be detected by our methods of analysis. 1C, without correction for ash, has nearly the same composition as 4A and 4B: a correction would tend to bring it into closer agreement. The amount of substance, however, was insufficient for an ash-determination.

As all the preparations analysed thus far were the insoluble modification of the proteid, a new extract was prepared. Five pounds of freshly-ground oats were boiled up with ten liters of alcohol of 0.915 sp. gr. The extract was pressed out, and added to another five pounds of oats and again heated to boiling. After filtering, a perfectly clear, deep ruby-red solution was obtained. This was concentrated by distillation on the water-bath to about one-third of its original volume. On cooling, a large amount of substance separated. This was thrown upon a filter and, after twenty-four hours, about seven-eighths of the solution had passed through. The filter, with its contents, was then boiled in ten liters of 60-per cent. alcohol, in a flask fitted with a reflux-condenser, for four hours. The substance entirely dissolved to a

clear, deep-red solution. The solution was then concentrated by distillation to about one-half, and cooled rapidly to 35° C., when it filtered readily. The precipitate formed a tough, jelly-like mass which did not adhere to the paper. It was boiled, as before, for several hours, with ten liters of 60-per cent. alcohol until completely dissolved. The perfectly clear solution was concentrated to one-half its volume, during which operation a large part of the substance deposited on the interior of the flask as a thick leather-like coating. This coating readily separated from the glass in large pieces of a dark-brown color. On cooling the liquid, a finely-divided yellowish precipitate appeared which did not settle out on standing. The muddy liquid was poured off and the leathery deposit was minced and treated with absolute alcohol, in order, if possible, to dehydrate the substance and render it pulverisable for analysis, but as it remained forty-eight hours without change, the attempt was abandoned. The substance suspended in the muddy liquid was now caused to separate by adding alcohol. After filtering, washing first with strong, then with absolute alcohol, the precipitate was united to the portion which had been digested with absolute alcohol, and the whole then boiled in two liters of 60-per cent. alcohol in a flask fitted with a return-condenser. After three hours' boiling, about one-half had dissolved. Two liters more of 60-per cent. alcohol were then added and the boiling continued. Considerable proteid still remained in a gelatinous form on the sides of the flask. The solution was filtered off and 1200 cc. of absolute alcohol were poured on the residual substance. This caused the jelly to break up into coarse lumps, whereupon 800 cc. of water were added, making two liters of 60-per cent. alcohol, and the boiling on the water-bath was continued for several hours. Some of the substance dissolved, the liquid was filtered, and the insoluble residue was treated for many days with absolute alcohol. It was then ground to a fine powder while still moist with alcohol, extracted with ether, and dried over sulphuric acid. This preparation, "7," weighed 9.1 grams.

The alcoholic solution filtered from the insoluble portion was concentrated to one-half and filtered, while hot, from the large amount of substance which had separated. The latter resembled raw rubber in appearance and consistence, but not in elasticity. It was finely minced, and, after having been digested with absolute alcohol, was pulverised, treated again with absolute alcohol,



washed with ether, and dried over sulphuric acid. This, "8," weighed 26 grams, and was a light powder of yellowish color. Unlike all the other preparations extracted from the oats by weak alcohol, which were analysed, 8 was still largely "uncoagulated" and soluble in that reagent.

These two preparations were analysed with the following results:

COAGULATED PROTEID.—*Directly extracted from Ground Oats by Weak Alcohol—7.*

	I.	II.	III.	I. Ash-free.
Carbon	52.98	...	...	53.10
Hydrogen	6.86	...	...	6.87
Nitrogen	16.34	16.41	16.39	16.39
Sulphur, Oxygen,	...	...	...	23.64
Ash	.25	...	...	...
				<hr/> 100.00

*Ash.*—1.007 grams air-dried substance (=0.9291 gram dried at 110° C.) gave 0.0023 gram ash = 0.25 per cent.

*Carbon and hydrogen.*—0.5076 gram, dried at 110° C., gave 0.9860 gram CO<sub>2</sub> = 52.98 per cent. C, and 0.3131 gram H<sub>2</sub>O = 6.86 per cent. H.

*Nitrogen, I* (Dumas' method).—0.5000 gram air-dried (=0.4606 gram dried at 110° C.) gave 64.1 cc. gas at 8° C. (barometer 750 mm. at 15° C.) = 16.54 per cent., less .20 found in blank = 16.34 per cent. N.

*Nitrogen, II* (Kjeldahl method).—0.5000 gram air-dried (=0.4606 gram dried at 110° C.) gave ammonia = 8.85 cc. HCl (1 cc. HCl = .00854 N) = 16.41 per cent.

III.—0.5000 gram air-dried (=0.4611 gram dried at 110° C.) gave ammonia = 8.85 cc. HCl = 16.39 per cent. N.

SOLUBLE PROTEID.—*Directly extracted from Ground Oats by Weak Alcohol—8.*

	I.	II.	III.	IV.	I. Ash-free.
Carbon	52.92	...	...	...	53.06
Hydrogen	6.93	...	...	...	6.94
Nitrogen	16.33	16.33	16.45	16.54	16.38
Sulphur	2.25	2.21	...	...	2.26
Oxygen	...	...	...	...	21.36
Ash	.24	...	...	...	...
					<hr/> 100.00

*Ash*.—1.0045 grams air-dried (=0.9027 gram dried at 110° C.) gave 0.0022 gram ash = 0.24 per cent.

*Carbon and hydrogen*.—0.4821 gram, dried at 110° C., gave 0.9356 gram CO<sub>2</sub> = 52.92 per cent. C, and 0.3003 gram H<sub>2</sub>O = 6.93 per cent. H.

*Nitrogen*, I (Dumas' method).—0.5000 gram air-dried (= 0.4554 gram dried at 110° C.) gave 63.1 cc. gas at 10° C. (barometer 759.5 mm. at 16° C.) = 16.53 per cent., less correction .20 = 16.33 per cent. N.

II.—0.5000 gram (=0.4490 gram dried at 110° C.) gave 62.42 cc. gas at 14° C. (barometer 770.3 mm. at 17° C.) = 16.53 per cent. N.; corrected = 16.33 per cent. N.

III. (Kjeldahl method).—0.5000 gram (=0.4490 gram dried at 110° C.) gave ammonia = 8.65 cc. HCl (1 cc. HCl = .00854 gram N) = 16.45 per cent. N.

IV.—0.5000 gram (=0.4490 gram dried at 110° C.) gave ammonia = 8.70 cc. HCl = 16.54 per cent. N.

*Sulphur*, I.—1.00 gram air-dried (=0.9107 gram dried at 110° C.) gave 0.1850 gram BaSO<sub>4</sub>, which, when fused with Na<sub>2</sub>CO<sub>3</sub> and reprecipitated, gave 0.1495 gram BaSO<sub>4</sub> = 0.020532 gram S = 2.25 per cent.

II.—1.00 gram (=0.9107 gram dried at 110° C.) gave 0.1575 gram BaSO<sub>4</sub>, which, when fused with Na<sub>2</sub>CO<sub>3</sub> and reprecipitated, gave 0.1469 gram BaSO<sub>4</sub> = 0.020175 gram S = 2.21 per cent.

These analyses are observed to agree closely with each other, as well as with several of the preparations obtained under various conditions from the first extract already described, as is shown by the following table:—

OAT-PROTEID EXTRACTED BY WEAK ALCOHOL.

	Soluble.	Coagulated					
	8.	7.-	1C. <sup>1</sup>	4A.	4B. <sup>1</sup>	4.	6A2. <sup>1</sup>
Carbon	53.06	53.10	52.66	53.09	53.12	...	...
Hydrogen	6.94	6.87	6.89	6.96	6.91	...	...
Nitrogen	16.38	16.39	16.32	16.56	16.52	16.27	16.40
Sulphur	2.26	23.64	24.13	23.39	23.45	...	...
Oxygen	21.36						
	100.00	100.00	100.00	100.00	100.00		

<sup>1</sup> Not corrected for ash.

The figures given by Kreusler for the nitrogen of two precipitates from his first alcoholic extract are likewise in close agreement with the above, *viz.* 16.22 and 16.21 per cent. From his "oat-legumin" Kreusler also extracted by means of alcohol a substance with 16.38 per cent. nitrogen.

It seems hardly probable that such concordant analyses could result from impure preparations or from a mixture of two or more proteids, especially in view of the varying conditions under which the preparations were obtained.

The very high content of sulphur is remarkable. No other analysis of a vegetable proteid approaches this amount. Ritt-hausen<sup>1</sup> found, indeed, in a single preparation from sesame press-cake 2.36 per cent., but he attributed this high percentage to some foreign substance precipitated with the proteid. He afterwards<sup>2</sup> stated the percentage of sulphur as 1.25, and ascribed the high figure first obtained to calcium sulphate. Among the animal-proteids besides *Keratin*, some forms of human *serum-albumin* contain 2.3 per cent. of sulphur.<sup>3</sup>

The fact that sulphur in my analyses is 0.60 per cent. more than found by Kreusler in his gliadin, indicates that his substance had undergone chemical change during the processes of preparation.

Ritthausen believes to have obtained from wheat-gluten by extracting with alcohol three distinct proteids, to which he applies the names *fibrin*, *gliadin*, and *mucedin*, and he includes under one or the other of these terms all the proteids soluble in alcohol which he and Kreusler found in their extended study of the cereals. That portion of wheat-gluten which is insoluble in alcohol Ritthausen denominated *gluten-casein*.

On the authority of Ritthausen, his names and the composition attributed by him to these substances have passed into chemical literature, and have superseded the various designations and analyses of the older investigators.

The proteid of the oat which I have obtained, soluble in alcohol, differs essentially, however, in composition from all these preparations of Ritthausen and Kreusler. Kreusler's analysis of mucedin from barley-grits alone fairly agrees with my results as respects carbon, hydrogen and nitrogen, but the same chemist's analysis of mucedin from barley-meal gives 0.84 per cent. higher nitrogen than that from grits, and but 0.68 per cent. sulphur.

<sup>1</sup> Pflüger's Archiv 21, 95 (1880).

<sup>2</sup> J. prakt. Chem. 26, 444.

<sup>3</sup> Starke; Jsb. thier. Chem. 11, 19.

In case of the other substances the discrepancies are still more decided. The properties and reactions given by Kreusler for the substance called by him *oat-gliadin* are true of the body just described, but these reactions mostly belong to proteids in general, or to the mucedin and fibrin of Ritthausen, and are not characteristic of any one body. Ritthausen states that on evaporating the alcohol solution of the gluten-fibrin prepared by him from wheat-gluten, a pellicle forms on the surface which renews itself as often as removed, and that neither mucedin nor gliadin shows this property. I have frequently observed the formation of films on evaporating solutions of the alcohol-soluble proteid from oats. This body, however, cannot be a mixture of Ritthausen's fibrin and gliadin, as its sulphur-content so largely exceeds theirs.

2. *Extraction with Alcohol after treatment with Water,—  
Preparation 9.*

Five pounds of oats were treated with water as long as any proteid was dissolved. The residue was then twice extracted with alcohol and strongly pressed. The first alcoholic extract was evaporated so far as to remove nearly all the alcohol. On cooling, the solution became turbid, and after standing deposited a brown, slimy substance exceedingly soluble in dilute alcohol. The liquid was decanted and the precipitate dissolved in dilute alcohol. After evaporating off the alcohol and cooling, the substance separated as before; the aqueous solution was decanted and the slimy residue treated with ether, which extracted a fatty oil from this material and caused it to assume a more solid consistence. The substance was then treated with alcohol of 93 per cent., which dissolved a little and converted the remainder into a solid lump, so that it could be transferred to a flask and digested with ether. By the continued action of ether the viscid substance was transformed into a loose, yellowish powder. After standing under ether for twenty-four hours, the body was filtered out and dissolved in dilute alcohol. This alcoholic solution was filtered and evaporated on the water-bath to a small volume. After cooling, the solution was poured from the gummy substance adhering to the dish, which was washed with water and repeatedly digested with absolute alcohol. As long as the substance retained water, a little dissolved during treatment with alcohol. The residue became granular and brittle, and was easily reduced to a fine

powder. When impregnated with absolute alcohol, the mass rapidly absorbed moisture from the air and became soft and viscid.

After thorough dehydration with absolute alcohol, the substance was rapidly filtered out and dried over sulphuric acid. It weighed 7.88 grams.

In testing the purity of this substance it was found to yield something to water. The whole preparation was, therefore, washed out completely with distilled water, and again treated with absolute alcohol and ether and dried over sulphuric acid. Analysis of this preparation, "9," gave the following results:

SOLUBLE PROTEID—*Extracted by Weak Alcohol from Ground Oats after treating them with Water—9.*

	I.	II.
Carbon	53.64	...
Hydrogen	6.88	...
Nitrogen	15.70	15.36
Sulphur	1.75	...
Oxygen	22.03	...
	<hr/> 100.00	

*Ash.*—0.6007 gram air-dried left no ash.

*Carbon and hydrogen.*—0.5886 gram, dried at 110° C., gave 1.1579 grams CO<sub>2</sub> = 53.64 per cent. C, and 0.3642 gram H<sub>2</sub>O = 6.88 per cent. H.

*Nitrogen, I* (Dumas' method).—0.5000 gram air-dried (= 0.4479 gram dried at 110° C.) gave 60.68 cc. gas at 8° C. (barometer 757 mm. at 12° C.) = 15.90 per cent. N, less .20 for blank = 15.70 per cent.

*II* (Kjeldahl method).—0.5000 gram air-dried (= 0.4479 gram dried at 110° C.) gave ammonia = 8.05 cc. HCl (1 cc. HCl = 0.00854 gram N) = 15.36 per cent.

*Sulphur.*—0.8958 gram, dried at 110° C., gave 0.1142 gram BaSO<sub>4</sub> = 0.0157 gram = 1.75 per cent. S.

3. *Extraction with Alcohol after treatment with Salt Solution—Preparations 10 and 11.*

Five pounds of oats were repeatedly treated with 10 per cent. solution of sodium chloride until nothing more was dissolved, and after pressing out as thoroughly as possible the residue was twice



treated with alcohol of 0.912 specific gravity, being pressed out each time, and the extracts kept separate. The first and second alcohol-extracts were united, evaporated on the water-bath until all alcohol had escaped, and the residue then cooled to 10° C. At this temperature the deposit formed brittle lumps which, after decanting the solution, were treated with ether and absolute alcohol. The lumps were thus brought into a granular state, in which condition the substance was treated for some time with ether until all fat had been removed. It was then dissolved in hot dilute alcohol, filtered and evaporated on the water-bath to a small volume. On cooling the proteid separated in a mass on the bottom of the dish. The aqueous liquid was poured off, and the residue treated with absolute alcohol and ether, whereupon it became brittle and was easily ground to a fine powder. This powder was washed with water until it no longer gave with silver nitrate a reaction for chlorine. It was then treated with absolute alcohol and dried over sulphuric acid. In appearance and behavior it resembled in all respects the substance extracted by alcohol after the oats had been treated with water. When analysed it was found to have the composition stated under "10."

The third alcoholic extract of the oats was treated in the same way, and the product obtained analysed with the following results, "11":

**SOLUBLE PROTEID**—*Extracted by Weak Alcohol from Ground Oats after treating them with Salt-solution—10 and 11.*

	10.			11.		
	I.	II.	III.	I.	II.	
Carbon	53.97	...	...	53.55	...	
Hydrogen	7.14	...	...	6.80	...	
Nitrogen	15.71	15.66	15.68	15.61	15.52	
Sulphur	1.80	...	...	} 24.04	...	
Oxygen	21.38	...	...			
	<hr/> 100.00			<hr/> 100.00		
Ash	0.56			0.25		

*Details of Analyses of 10.*

*Ash.*—1 gram air-dried (= 0.9361 gram dried at 110° C.) gave 0.0053 gram ash = 0.56 per cent.

*Carbon and hydrogen.*—0.3443 gram, dried at  $110^{\circ}$  C., gave 0.6780 gram  $\text{CO}_2$  = 53.70 per cent. C, and 0.2200 gram  $\text{H}_2\text{O}$  = 7.09 per cent. H.

*Nitrogen*, I (Dumas' method).—0.5000 gram air-dried (= 0.4681 gram dried at  $110^{\circ}$  C.) gave 60.47 cc. gas at  $8^{\circ}$  C. (barometer 772 mm. at  $8^{\circ}$  C.) = 15.80 per cent., less .20 for blank = 15.60 per cent. N.

II (Kjeldahl method).—0.5000 gram air-dried (= 0.4681 gram dried at  $110^{\circ}$  C.) gave ammonia = 8.53 cc.  $\text{HCl}$  (1 cc.  $\text{HCl}$  = 0.00854 gram N) = 15.57 per cent. N.

III.—0.5000 gram gave ammonia = 8.55 cc.  $\text{HCl}$  = 15.59 per cent. N.

*Sulphur.*—1 gram air-dried substance (= 0.9361 gram at  $110^{\circ}$  C.) gave 0.1232 gram  $\text{BaSO}_4$  = 0.0169 gram = 1.80 per cent.

#### *Details of Analyses of II.*

*Ash.*—0.8680 gram, dried at  $110^{\circ}$  C., gave 0.0022 gram ash = 0.25 per cent.

*Carbon and hydrogen.*—0.3676 gram, dried at  $110^{\circ}$  C., gave 0.7190 gram  $\text{CO}_2$  = 53.42 per cent. C, and 0.2242 gram  $\text{H}_2\text{O}$  = 6.78 per cent. H.

*Nitrogen*, I (Kjeldahl method).—0.5000 gram (= 0.4715 gram dried at  $110^{\circ}$  C.) gave ammonia = 8.60 cc.  $\text{HCl}$  (1 cc.  $\text{HCl}$  = 0.00854 gram N) = 15.59 per cent N.

II.—0.5000 gram (= 0.4715 gram dried at  $110^{\circ}$  C.) gave ammonia = 8.55 cc.  $\text{HCl}$  = 15.49 per cent. N.

#### 4. *Extraction with Alcohol after treatment with Water and Salt-solution,—Preparation 12.*

Five pounds of oats were extracted with water, and then with 10 per cent. salt-solution as long as anything was removed. The residue was twice digested with alcohol of 0.9 sp. gr., the two alcohol extracts were united and concentrated to a small volume on the water-bath. After cooling, the substance which deposited was filtered out and dissolved in dilute alcohol. The filtered solution was evaporated until nearly all the alcohol was expelled, and finally poured into cold water. The abundant precipitate thus produced settled rapidly, forming a pasty mass on the bottom of the dish, from which the water could be completely

decanted. By treatment with ether and absolute alcohol the substance was rendered dry and brittle, and was easily ground to a yellowish powder. This was transferred to a flask and digested for twenty-four hours with a mixture of absolute alcohol and ether, then washed with ether to remove the alcohol, and dried in the air. The product weighed 12 grams. After dissolving this preparation in dilute alcohol and evaporating to a small volume on the water-bath, the concentrated solution was poured into a liter of cold distilled water. The substance thus precipitated was washed by decantation with distilled water until all chlorides had been removed, then treated with absolute alcohol and ether and dried over sulphuric acid. This preparation was found to have the following composition :

SOLUBLE PROTEID—*Extracted by Weak Alcohol from Ground Oats after treating them with Water and with Salt-solution—"12."*

	I.	II.
Carbon	53.63	...
Hydrogen	7.16	...
Nitrogen	15.83	15.86
Sulphur	1.74	...
Oxygen	21.64	...
	<hr/>	
	100.00	
Ash,	0.11	

*Ash.*—0.7593 gram, dried at 110° C., gave 0.0008 gram ash = 0.11 per cent.

*Carbon and hydrogen.*—0.2850 gram, dried at 110° C., gave 0.5595 gram CO<sub>2</sub> = 53.58 per cent. C, and 0.1836 gram H<sub>2</sub>O = 7.15 per cent. H.

*Nitrogen, I* (Dumas' method).—0.4168 gram, dried at 110° C., gave 56.95 cc. N at 18° C. (barometer 764.5 mm. at 22° C.) = 15.81 per cent.

*II* (Kjeldahl method).—1.0183 grams, dried at 110° C., gave ammonia = 19.63 cc. HCl (1 cc. HCl = 0.00822 gram N) = 15.84 per cent.

*Sulphur.*—0.9682 gram, dried at 110° C., gave 0.1218 gram BaSO<sub>4</sub> = 0.01673 gram S = 1.74 per cent.

*Recapitulation.*

The following statement brings together the analyses of the four preparations last described.

## PROTEID EXTRACTED FROM OATS BY WEAK ALCOHOL.

After treatment of the meal with—

	Water. 9.	Salt-solution. 10.      11.		Water and Salt-sol. 12.	Average.
Carbon	53.64	53.97	53.55	53.63	53.70
Hydrogen	6.88	7.14	6.80	7.16	7.00
Nitrogen	15.70	15.71	15.61	15.83	15.71
Sulphur	1.75	1.80	} 24.04	1.74	1.76
Oxygen	22.03	21.38		21.64	21.83
	100.00	100.00	100.00	100.00	100.00

When the above analyses are compared, as below, with those of the preparations obtained without previous treatment of the oats with water or salt-solution, it is evident that we have in hand two quite different and distinct substances, neither of which agrees in composition with Kreusler's *Oat-Gliadin*.

## PROTEID EXTRACTED FROM OATS BY WEAK ALCOHOL.

	Without Action of Water or Salt-solution. 8.	After Action of Water or Salt-solution. Average.
Carbon	53.06	53.70
Hydrogen	6.94	7.00
Nitrogen	16.38	15.71
Sulphur	2.26	1.76
Oxygen	21.36	21.83
	100.00	100.00

The differences in behavior of the two substances are much more marked than those of composition. The body extracted by alcohol without the previous treatment with water, becomes insoluble in alcohol with great readiness, and, after having been dissolved and precipitated a few times, is again dissolved very slowly and only in a large amount of hot alcohol of 0.9 sp. gr. When wet with absolute alcohol it can be exposed to moist air without becoming gummy.

On the other hand, the body extracted by alcohol after the action of water or 10-per cent. salt-solution shows no tendency to

become insoluble, even after long heating with very dilute alcohol. It is freely soluble even in cold alcohol of 0.9 specific gravity, and, when wet with absolute alcohol, immediately attracts moisture from the air, becoming sticky and viscid. In appearance the two bodies do not materially differ, both being light, yellowish powders, when prepared as described.

Both these substances are soluble in dilute acids and alkalies to solutions from which on neutralisation they precipitate, retaining their solubility in dilute alcohol.

The fact that weak alcohol acts as a solvent for these bodies, which are insoluble in either pure (absolute) alcohol or pure water, is doubtless due to the formation of hydrates that, while insoluble in water, are soluble in alcohol, but that cannot exist in strong alcohol, being thereby dehydrated.

The proteid whose composition is expressed by analysis 8 was first obtained by Norton, who extracted ground oats directly with hot alcohol, distilled the solution carefully to dryness, dissolved out the oil by ether and the salts and sugar by water. Norton designated this body *Glutin*, and considered it "analogous to the gluten of wheat"; he states that the preparation which he thus separated and weighed was no longer soluble in alcohol, but he did not attempt any further investigation of its properties or composition.<sup>1</sup>

Von Bibra, who found in oats 3 per cent. of *Plant-gelatin* (Pflanzenleim), does not describe its mode of preparation, but states that it contained 15.6 per cent. of nitrogen.

Kreusler indeed extracted crushed oats directly by 80 per cent. alcohol, and in his first preparations found 16.22 and 16.21 per cent. of nitrogen; but the substance, from whose analysis he decided upon the composition of *Oat-gliadin*, had been "purified" by dissolving in acetic acid and precipitating by potash solution, and, according to his results, contained 1.3 per cent. more nitrogen, 0.65 per cent. more hydrogen, and 0.6 per cent. less sulphur than exist in either of the proteids soluble in alcohol which I have analysed.

It would be premature to attempt a revision of the nomenclature of these proteids until after re-investigation of the proteids soluble in alcohol derived from the other cereals.

(*To be concluded.*)

<sup>1</sup> Am. J. Sci. [2] 3, 229.



Contributions from the Chemical Laboratory of Purdue University.

## V.—A NEW SOURCE FOR XYLOSE.

BY W. E. STONE AND DUMONT LOTZ.

One of us, in applying the furfurol test to a variety of vegetable materials, in search of the pentose carbohydrates, or *pentans*, found that the "cobs" of Indian corn were especially rich in these bodies.<sup>1</sup>

In the preliminary test cited, by distilling the air-dried material with sulphuric acid of 1.254 specific gravity, and precipitating the furfurol thus obtained as furfuramide, the equivalent of twelve to thirteen per cent. of furfurol was obtained. This result, which quite equals that obtained under similar conditions from cherry gum and gum tragacanth, indicated that the corn "cobs" might compare favorably with the latter materials as a source of one or the other of the pentoses. Since the tests mentioned we have repeated the furfurol determinations, making use of a method proposed by Tollens and Chalmot, and privately communicated to one of us. By this method the material is distilled with hydrochloric acid of 1.06 specific gravity, the furfurol thus obtained is precipitated from acetic-acid solution with phenyl-hydrazine, dried in a current of dry air at 60°, and weighed as phenyl-furfurazide. In this way somewhat higher results were obtained. One distillation of the air-dried material gave 21.89 per cent. furfurol, and a second, 22.36 per cent.

Our method of procedure was to extract the pentose carbohydrates from the material by means of strong alkalies, and then by hydrolysis convert them into the specific pentose.

Two and one-half kilos. of finely-ground air-dried "cobs" were digested, cold, with twelve liters of one-per cent. ammonia solution during about thirty hours, for the purpose of removing coloring matters. When drawn off the liquid was of a dark-brown color, but nothing was precipitated from it when several volumes of strong alcohol were added, showing that none of the gummy pentose carbohydrates had been extracted.

The residue, which was perceptibly lighter in color than before this treatment, was next subjected to the action of a sodium hydroxide solution in order to effect solution of the gums. In

<sup>1</sup> This Journal 13, 73.

his treatment of sugar-beet chips for the extraction of the so-called metapectic acid from which arabinose was first prepared, Scheibler used for this purpose quicklime.<sup>1</sup> Later, one of us by the same process obtained from the fermented residue of malt a gum which, upon hydrolysis, yielded both arabinose and xylose.<sup>2</sup>

Tollens and Allen have found, however, that caustic alkalies gave better results in the preparation of xylose from wheat-straw.<sup>3</sup>

Accordingly, the residue left after extraction with ammonia received enough of a two-per cent. sodium hydroxide solution to cover it, and the whole was boiled during eight hours, the liquor becoming very dark-colored and mucilaginous. After standing eight hours longer the liquid was separated from the residue of fibre and insoluble matter by means of a press. Upon addition of two volumes of 95-per cent. alcohol to this liquor, a voluminous, dark-brown, gummy precipitate was thrown down. This was several times washed with alcohol by decantation. Finally it was redissolved in a little water to which some hydrochloric acid had been added, and then reprecipitated with alcohol. This treatment was repeated several times. The final result was an amorphous substance of light-brown color, which upon exposure to the air seemed slightly hygroscopic, and rapidly blackened. After drying over sulphuric acid this product weighed about 200 grams, or about eight per cent. of the material employed.

A small quantity of this gum was repeatedly dissolved in water and reprecipitated from an acid solution by means of alcohol, with the object of obtaining a pure ash-free product for further study. The last traces of ash were, however, very difficult to remove, and after some months the preparation still contained 0.76 per cent. Spectroscopic examination showed this ash to consist of sodium salts. Two portions of this gum yielded on distillation, respectively, 48 and 50 per cent. of furfural. This partially-purified material was noteworthy for its solubility in water and its rapid discoloration on exposure to the air. The greater portion of the 200 grams of gum was heated in a flask with two liters of two-per cent. sulphuric acid for twelve hours, an inverted condenser being used to prevent concentration of the acid by evaporation. At the end of this time about 50 grams of amorphous, insoluble matter remained in the flask. The acid liquor was filtered from this

<sup>1</sup> Ber. d. chem. Ges. **1**, 58, 108.

<sup>2</sup> Ann. Chem. (Liebig) **249**, 243.

<sup>3</sup> Ibid. **260**, 289.

residue, neutralised with calcium carbonate, and evaporated to a thick syrup. Upon adding about three volumes of strong alcohol to this and boiling, a dark-brown, tasteless gum was precipitated and removed, and the liquid after concentration yielded slowly a mass of dark-colored crystals.

After repeated washings and recrystallisations, two successive portions of crystals were obtained, which were nearly white, sweet to the taste, and reduced Fehling's solution strongly. In all about six grams of this product were obtained, or nearly three per cent. of the 200 grams of gum used. Probably an equal amount of sugar remained in the dark-colored and non-crystallisable mother-liquors. The amount of this product obtained was disappointingly small in view of the promising preliminary indications. The syrups obtained after hydrolysis, however, contained much unchanged gummy matter, and crystallised only slowly and with great difficulty. It was also found subsequently that the extracted cobs still contained a very large amount of the furfural-producing bodies. The caustic soda had evidently extracted only a very small amount of the *pentans*, or pentose gums, which accounts for the small yield of sugar. To characterise the product thus obtained, the specific rotation was determined, and its phenyl-hydrazine derivative prepared. Of the two portions of crystals, No. 1 showed the specific rotation  $(\alpha)_D = 19.4^\circ$ ; No. 2,  $(\alpha)_D = 19.7^\circ$ . These numbers agree with sufficient accuracy with the specific rotation of xylose— $(\alpha)_D = 18.5^\circ$  to  $19^\circ$ —to identify both products as xylose, and show that this was the only pentose present. The phenyl-hydrazine compound was prepared in the usual way, had a normal appearance and behavior, and showed the melting-point  $159^\circ$ —the approximate melting-point observed for phenyl-xylosazon ( $156^\circ$ – $160^\circ$ ). In distinction from the phenyl-arabinosazon, which has the same melting-point, this compound was distinctly laevo-rotatory, a property of the xylose derivative as shown by Fischer.<sup>1</sup>

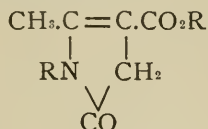
These data add a new and, as we hope to show by a repetition of the above work, a fruitful source of xylose to those already known, and emphasise once more the reliability of the furfural test for the recognition of such materials.

<sup>1</sup> Ber. d. chem. Ges. 23, 355.

ON THE ACTION OF AMMONIA AND ANILINE ON  
 $\alpha$ -ACETO-GLUTARIC ETHER.

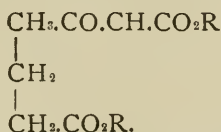
BY WILLIAM ORREN EMERY.

In a recent paper<sup>1</sup> I described a method by which unsaturated  $\gamma$ -lactams of the general formula

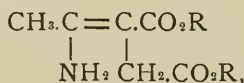


could easily be prepared. It was found that the amido- and alkylamido-derivatives of aceto-succinic ether, under certain conditions, lose the elements of alcohol, and are thereby changed into unsaturated  $\gamma$ -lactams.

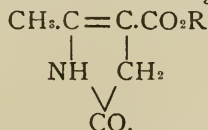
It now seemed desirable to study the action of ammonia and amine bases on some  $\delta$ -ketonic ether, and to this end I chose  $\alpha$ -aceto-glutaric ether,



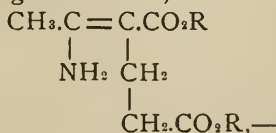
Ammonia and aceto-succinic ether yield  $\alpha$ -amido-ethylidene-succinic ether,



which can with comparative ease be changed into the lactam



Now if it were possible by the action of ammonia on  $\alpha$ -aceto-glutaric ether to prepare a similar amido-derivative—for example,  $\alpha$ -amido- $\alpha$ -ethylidene-glutaric ether,



<sup>1</sup> This Journal 13, 85.

it might reasonably be expected that such a compound, having the amido-rest in the  $\delta$ -position to the one carboxyl group, would show even a greater tendency to go over into a lactam. Experiment has shown, however, that such is not the case; only in two instances was it possible, by the action of ammonia and aniline on  $\alpha$ -aceto-glutaric ether, to prepare bodies which have apparently the lactam constitution: the intermediate substances formed have not as yet been isolated.

Although the alkyl amines react readily with  $\alpha$ -aceto-glutaric ether, I did not succeed in separating the new products in a pure condition, owing to the slight difference between the boiling-points of the latter and of the unchanged ether.

#### *Ammonia and $\alpha$ -Aceto-glutaric Ether.*

One volume of  $\alpha$ -aceto-glutaric ether was mixed with two volumes of concentrated alcoholic ammonia. After allowing the mixture to stand 24 hours in a cool place, it was poured into a shallow dish, in order that the alcohol might slowly evaporate at the ordinary temperature. As the residual liquid showed no signs of crystallisation, it was next distilled under greatly diminished pressure. After considerable unchanged  $\alpha$ -aceto-glutaric ether had passed over, a very small quantity of crystals distilled, or rather sublimed, over, while the residue in the distilling flask crystallised on cooling. The crystals were first freed from an oily substance by drying on porous plates, then recrystallised twice from a mixture of chloroform and ether. Small, white crystals were obtained, which melted at  $156^\circ$ , and upon analysis gave the following figures:

I. 0.1512 gram substance gave 0.3255 gram  $\text{CO}_2$  and 0.0963 gram  $\text{H}_2\text{O}$ .

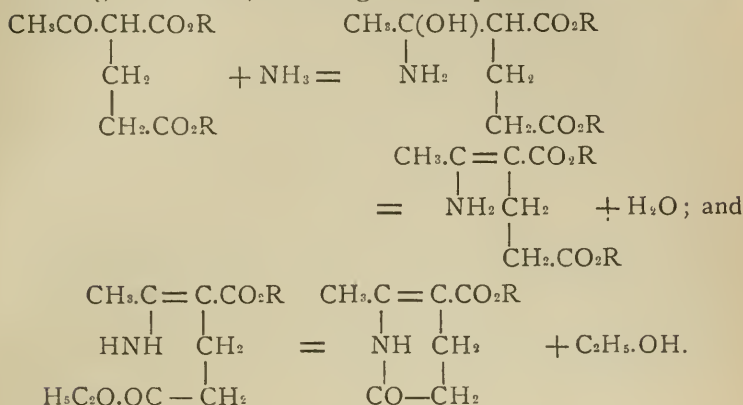
II. 0.2139 gram substance gave the following data:  $B = 767.5$ ;  $t = -1.5^\circ$ ;  $v = 13$  cc.

	Calculated for $\text{C}_9\text{H}_{13}\text{NO}_3$ .	Found.	
		I.	II.
C	59.02	58.71	...
H	7.10	7.08	...
N	7.65	...	7.71
O	26.23	...	...

The new compound has therefore the formula  $\text{C}_9\text{H}_{13}\text{NO}_3$  and



is probably the last product arising by the action of ammonia on  $\alpha$ -aceto-glutaric ether, according to the equations



The new substance may be regarded as the lactam of  $\alpha$ -amido- $\alpha$ -ethylidene-glutaric ether. It is quite readily soluble in chloroform, less so in ether.

*Aniline and  $\alpha$ -Aceto-glutaric Ether.*

Aniline and  $\alpha$ -aceto-glutaric ether were mixed in the proportion of equal molecular-weights. After allowing the mixture to stand for several days, it was distilled in a vacuum. Unchanged aniline and ether passed over, leaving a residue in the distilling-flask; upon treating this residue with ether it gradually solidified to a mass of fine crystals. These were first freed from an accompanying oil by drying on porous plates, then recrystallised twice from a mixture of chloroform and ether. Fine, white crystals were obtained, which melted at  $196^\circ$ – $197^\circ$ , and on analysis gave the following numbers:

I. 0.1406 gram substance gave 0.3586 gram  $\text{CO}_2$  and 0.0862 gram  $\text{H}_2\text{O}$ .

II. 0.2640 gram substance gave the following data:  $B=761$ ;  $t=7^\circ$ ;  $v=13$  cc.

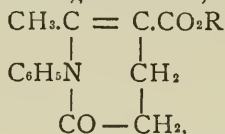
	Calculated for $\text{C}_{16}\text{H}_{17}\text{NO}_2$ .	Found.	
C	69.50	69.55	...
H	6.56	6.81	...
N	5.40	...	5.97
O	18.53	...	...

From the above it is evident that the new substance is formed

from equal molecules of aniline and  $\alpha$ -aceto-glutaric ether, according to the equation



The new compound has, in all probability, a constitution analogous to that of the preceding substance, namely—



and may be regarded as the lactam of  $\alpha$ -phenyl-amido- $\alpha$ -ethylidene-glutaric ether. It is easily soluble in chloroform; with difficulty in ether.

CHEMICAL LABORATORY, BONN UNIVERSITY, *February, 1891.*

## THE ATOMIC WEIGHT OF OXYGEN.

BY W. A. NOYES.

In a recent number of this Journal<sup>1</sup> Dr. E. H. Keiser has pointed out a source of error in my determinations of the atomic-weight of oxygen. In order to determine how far the error in question can have affected the result which was obtained, the following experiments have been made:

Ten grams of caustic potash, from the same dealer and of the same grade as that used in my work last year, were placed in a small bulb, which was then sealed to a tube bearing a stop-cock. To the other end of the tube was sealed a second bulb, which could be connected with a Sprengel pump. The whole was then exhausted and the stop-cock closed. Twelve to fifteen cubic centimeters of water were placed in the upper bulb and the latter was again exhausted. By continuing the action of the pump at intervals for one or two hours, most of the air dissolved in the water was removed. On opening the stop-cock the water ran down into the bulb containing the caustic potash. The gases evolved by the solution of the latter in the water were pumped out and analysed. They consisted in one experiment of 0.42 mg. of nitrogen and 0.10 mg. of oxygen; in a second experiment, of 0.63 mg. of nitrogen and 0.16 mg. of oxygen.

<sup>1</sup> This Journal 13, 253.

From the amount of caustic potash used in my drying tubes, it is impossible that more than three or four grams of caustic potash could have passed into solution in the course of any single determination. It seems to be certain, therefore, that the amount of oxygen, from this source could not have exceeded, on the average, one-tenth of a milligram for each determination, and was probably decidedly less than that. One-tenth of a milligram of oxygen, if present, would cause an error of 0.002 H in my final result, or, if a correction were applied, it would raise the value from 15.896 to 15.898.

It may be remarked, further, that the fact that the oxygen coming from the caustic potash is always associated with several times its weight of nitrogen, taken in connection with the amounts of nitrogen which were found in my hydrogen, proves that the hydrogen could not have been seriously contaminated from this source.

Dr. Keiser suggests that there are other sources of error in my work. I am well aware that this is the case, and I sincerely hope that errors which I may have overlooked, or whose importance I may have underestimated, may be pointed out. My desire is the same as that of all other chemists—that we may soon have an accurate and established value for the constant in question.

It is with extreme reluctance that I refer at all to the remarks with which Dr. Keiser opens his communication. Morley has shown that dry air can not be passed through a rubber connection without taking up water. In the sketch of his apparatus which Dr. Keiser has given,<sup>1</sup> he represents the oxygen and air as passing through several inches of rubber tubing before entering the phosphorus pentoxide tube to which I have referred. It would seem, then, not a transgression of the truth to say that an error must have been introduced when the assumption was made that *all* of the gain in weight of that tube came from water in the hydrogen which was passed through it. It is entirely possible that I have overestimated the importance of this error. The only positive statement which I had made, however, is that an error has been pointed out; even that statement was qualified in one of the papers which have been referred to by Dr. Keiser.

ROSE POLYTECHNIC INSTITUTE, *April*, 1891.

<sup>1</sup> Am. Jour. of Sci. **34**, 200.

## REVIEWS AND REPORTS.

THE ISOMERIC BENZENE HEXACHLORIDES.<sup>1</sup>

Before considering the two articles by Friedel and by Matthews which call forth this article, a brief review of the literature of the subject may not be out of place.

The ordinary benzene hexachloride,  $C_6H_6Cl_6$ , was first studied by Faraday and by Mitscherlich, and is a substance crystallising in clinorhombic prisms and fusing at  $157^\circ$ . In 1884 Meunier<sup>2</sup> found that benzene hexachloride formed by the action of chlorine on boiling benzene in the sunlight, contains a small amount of an isomer fusing and subliming at about  $310^\circ$ , and crystallising in regular octahedra. In the same year Schüpphaus<sup>3</sup> published an article in which he showed that he had obtained the same substance somewhat before Meunier, but had supposed it to be diphenyl dodekachloride,  $C_{12}H_{10}Cl_{12}$ . Schüpphaus gave his crystals to Dr. H. Söffing for crystallographic examination; they were found to be regular octahedra, and identical with the substance obtained by Meunier. Paterno and Nasini<sup>4</sup> in 1888 determined the molecular-weight of the two chlorides by Raoult's method, and found both to have the formula  $C_6H_6Cl_6$ .

Matthews, in the paper referred to, in studying the simultaneous action of chlorine and sodium hydroxide on organic compounds, found that when chlorine is conducted into a 1-per cent. solution of sodium hydroxide on which benzene is floating, the benzene is converted into a heavy yellow oil, which in a few hours deposits colorless crystals, and on further treatment with chlorine is almost completely changed to benzene hexachloride. He finds that the presence of the sodium hydroxide increases the yield of hexachloride, equally good results being obtained in sunlight or darkness. When recrystallised several times from 80-per cent. acetic acid, the substance fuses at  $157^\circ$ , but a portion is left unfused; he recognises in this Meunier's  $\beta$ -chloride, and tries various methods of separation, among others Meunier's, which consists in boiling the crude chloride with alcoholic potassium cyanide for 30 hours. This treatment completely decomposes the  $\alpha$ -compound and does not decompose the more stable  $\beta$ -chloride, which is extracted with alcohol and purified by sublimation. Matthews finally found that if the crude chlorides be distilled in a current of steam, the  $\alpha$ -chloride is volatile, the  $\beta$ - remains behind: the separation is complete. On

<sup>1</sup> C. Friedel: Sur les hexachlorures de benzène; Bull. Soc. chim. (Paris) [3] 5, 130. F. E. Matthews: The  $\alpha$ - and  $\beta$ -Modifications of Benzene Hexachloride; J. Chem. Soc. 1891, 165.

<sup>2</sup> J. Meunier: Bull. Soc. chim. (Paris) [2] 41, 530.

<sup>3</sup> Schüpphaus: Ber. d. chem. Ges. 17, 2256.

<sup>4</sup> Gazz. chim. ital. 19, 195; reviewed in Ber. d. chem. Ges. 22, Referate, 643-4.

recrystallising the  $\beta$ -derivative a single time from alcohol, he finds it pure; the  $\alpha$ -derivative recrystallised from alcohol or acetic acid is also found to be quite pure and free of the  $\beta$ -. He shows the  $\alpha$ -chloride to be insoluble in water, easily soluble in ordinary organic solvents; very stable—not acted on by fuming nitric acid, chromic acid, ammonia, or boiling silver nitrate—; alcoholic potash and potassium cyanide decompose it; when heated above its melting-point it loses hydrochloric acid. The molecular-weight determination by Raoult's method confirmed the results of Paterno. The  $\alpha$ -chloride forms about 70 per cent. of the crude chlorides.

The  $\beta$ -modification is extremely stable. Boiling alcoholic potassium cyanide does not affect it; it must be boiled for three hours with alcoholic potash to insure decomposition; it is much less soluble than the  $\alpha$ -, but the two cannot be separated satisfactorily by fractional crystallisation. The molecular-weight determination (Raoult) gives the formula  $C_6H_6Cl_6$ , as found by Paterno. Both modifications, boiled with alcoholic potash, yield the same trichlorobenzene.

While Matthews has increased our knowledge of the subject, through his improved method of making the crude hexachlorides and his quantitative separation of the two modifications, M. Friedel in his paper discusses in a remarkably ingenious way the constitution of the two hexachlorides, in the light of the stereochemical hypothesis. The paper is closely condensed, and it seems best in some parts of it simply to translate the author's words. He refers first to the application of Le Bel and Van't Hoff's theory to Kekulé's benzene-formula, by which, supposing that the simple union of two carbon atoms is expressed by the contact of two tetrahedra at an apex of each, and that double union of two carbon atoms is expressed by the coincidence of an edge of each of two tetrahedra, we obtain a figure like the following:

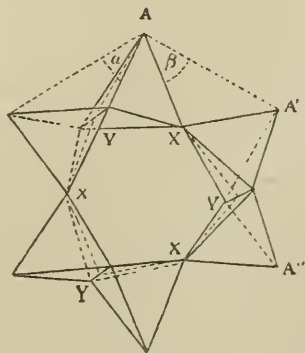


FIG. 1.



Friedel thinks that the well-known objection made to the Kekulé formula—that it admits the possibility of two ortho-derivatives of benzene—can be disposed of by the very simple assumption that the action of an atom of hydrogen—or of a group replacing it—on other atoms depends on the *distance*, all other conditions being equal. Now, in benzene, according to the Kekulé formula, each atom of hydrogen is joined to an atom of carbon, which is itself joined by one valence to an exactly similar atom of carbon, and by two valences to another; the hydrogen atoms are then in exactly the same conditions, and it seems fair to assume that if the *distances* separating them, *i. e.*, the distances between the free apices of the tetrahedra, are *equal*, the reciprocal action will be equal.

It is easy to satisfy this condition in a figure formed by three groups of two tetrahedra each—the two tetrahedra having a common edge, and each group being united to the two other groups by one valence; this being Kekulé's formula merely expressed stereo-chemically.

Calculation shows that the free apices of the tetrahedra will be equidistant when the edges of the hexagon formed by joining these apices form with those edges of the tetrahedra lying in the same plane the angles  $\beta = 39^\circ 1' 58''$ ; and when the intersections of the same plane with those exterior faces of the tetrahedra normal to the plane *P* form the angles  $\alpha = 26^\circ 14'$  (Fig. 1). In this case the angles of the symmetric hexagon formed by the intersections of the plane containing the free apices of the tetrahedra, with the interior faces of the tetrahedra normal to this plane, will be  $148^\circ 36'$  at the angles *XXX*, where there is simple union, and  $91^\circ 24'$  at the points *YYY*, where there is double union. A figure of this kind satisfies the conditions demanded, *i. e.*, *equal distances between the atoms of hydrogen*, each of which is otherwise under exactly similar conditions. If this be granted, there is no possibility for the formation of two ortho-derivatives of benzene.

The figure thus obtained is one of great symmetry, and it should be noticed that the successive tetrahedra deviate but little from the position which would be normal in the case of two tetrahedra joined by simple union, inasmuch as the line which would seem to be the line of attraction for two tetrahedra united by an apex—that is, by simple union—is that which passes from the apices to the centres of gravity of the bases, *i. e.*, the lines of the ternary axes of the cube, which form with the edges of the tetrahedron angles of  $35^\circ 16'$ . The deviation from this line in our figure is but  $3^\circ 16'$  for each of the tetrahedra.

With the double bonds, the attractive force would be exercised in the plane bisecting the dihedral angles of two tetrahedra united by a common edge. The deviation is here a little greater, *i. e.*,  $9^\circ$  for each tetrahedron. These deviations are but trifling in relation to so nearly perfect a symmetry.

Assuming this symbol for benzene, it is easy to see that in the formation of addition-products the double bond will be broken, as in the fatty series, and that in consequence, on adding two atoms of chlorine, those edges of the two tetrahedra which were in contact will fall into the plane which passes through the simple bonds, while those edges which bear each one atom of hydrogen and one atom of chlorine will fall at a right angle to this plane, in such manner that the two chlorine atoms are on the same side of the plane—in the *cis* position, to adopt Bayer's terminology.

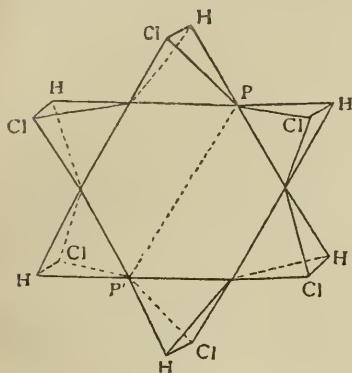


FIG. 2.

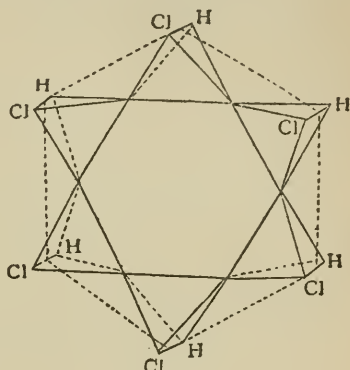


FIG. 3.

Following out this reasoning, we see that only two compounds can be formed by adding three molecules of chlorine to benzene, one *trans*, the other *cis*, as shown in Figs. 2 and 3. In the *trans*, four atoms of chlorine, attached to four adjacent carbon atoms, are on one side of the plane of the molecule, and the two other atoms on the other side.

It is to be noted that, supposing nothing causes the double bond to break preferably on one or the other side of the plane, there will always be one part of the *cis* isomer formed to three parts of the *trans*. For, after the first molecule of chlorine is fixed, the second may be placed on the same side of the plane, or on the other; and, other conditions being equal, will yield as much tetrachloride of the *cis* as of the *trans* modification. The *third* molecule of chlorine, reacting with the *cis* tetrachloride, will form as much hexachloride of the *cis* as of the *trans* variety, but, reacting with the *trans* tetrachloride, it can form only the *trans* hexachloride;—or, summed up, *one part cis to three parts trans*.

Of course these conclusions—which would hold strictly if the products formed by the action of chlorine were enantiomorphous, differing only in rotatory power—cannot hold strictly where, as in the present case, the isomeric bodies differ greatly, both in their structure and properties. Still, the action of chlorine on the interme-

diate products formed may sometimes be very slight, so that this reasoning may give an approximate idea of what takes place. M. Friedel goes on to say that he has obtained from the crude hexachloride—by fractional crystallisation with chloroform—1 part of octahedric hexachloride to 4 or to  $3\frac{1}{2}$  parts of the clinorhombic modification. It will be remembered that Matthews, by his better method of separation, obtained 70 per cent.  $\alpha$ - to 30 per cent.  $\beta$ -, which is still nearer to the proportion suggested by Friedel. The latter argues that the octahedral  $\beta$ -modification is *cis* because of the proportion in which it is formed, and because the greater symmetry of the *cis* structure may account for the comparative stability, greater density, and higher boiling-point of the octahedral variety.

Friedel thinks that the coincidence in these substances between the crystalline symmetry and the molecular symmetry cannot be accidental, for, on examining Fig. 2, it will be seen that the molecule of the  $\alpha$ -hexachloride has a clinorhombic symmetry, and admits of only one plane of symmetry, the trace of which on the plane of the simple bonds is *PP'* to which the one axis of symmetry is perpendicular: the  $\alpha$ -hexachloride crystallises in clinorhombic prisms.

Meunier described his hexachloride as crystallising in regular octahedra without action on polarised light. It is true that, when it is crystallised from benzene or chloroform, octahedra having exactly the appearance and angles of regular octahedra are formed; but M. Friedel finds by careful study that these octahedra are made up by grouping eight pyramids having for bases the faces of the octahedra, their apices being united in the centre of the crystal. He finds that these crystals act on polarised light; he considers it certain that they belong in the category of the pseudo-regular substances studied by Mallard, where the octahedra are formed by grouping eight triangular pyramids belonging to the rhombohedric or hexagonal system.

Now, as shown in Fig. 3, the symmetry of the molecule of the  $\beta$ -benzene hexachloride is, as is suggested by a consideration of his hypothesis, an hexagonal symmetry.

E. RENOUF.

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#### CORRECTION.

✓ Page 160, No. 3, line 13 from bottom: After " $\beta$ -ethoxy-naphthalene" insert "Thirty grams of the  $\beta$ -diazo-naphthalene sulphate yielded six grams of  $\beta$ -ethoxy-naphthalene and only one gram of naphthalene, which is equivalent to a conversion of about thirty per cent. of the diazo compound into  $\beta$ -ethoxy-naphthalene, and seven per cent. into naphthalene."

# AMERICAN CHEMICAL JOURNAL.

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## A SYSTEMATIC STUDY OF THE ACTION OF DEFIN- ITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

BY WOLCOTT GIBBS, M. D., *Rumford Professor (Emeritus) in Harvard University*, AND EDWARD T. REICHERT, M. D., *Professor of Physiology in the University of Pennsylvania*.

(Continued from p. 307, Vol. XIII.)

### *Nitroprusside of Sodium.*

In the frog this salt produces sluggishness, jerkings, convulsive movements, a diminution of reflex activity, slowing of the respirations and heart-beats, a diminution of sensibility, loss of voluntary motion and, finally, death. The muscles and sensory nerves are depressed, but the motor nerves are not affected. The alterations in reflex excitability are due in part to the action on the sensory nerves, but chiefly to a direct action on the spinal cord. The convulsive movements are spinal in origin.

Given to the dog by the stomach in the dose of 0.2 gram per kilo., there is noted vomiting, salivation, muscular weakness, diminution and loss of tactile sensibility, defecation, unconsciousness, and slight tremors. The respirations are increased, the temperature falls decidedly, the pulse is at first increased, then diminished, clonic or tetanic convulsions may occur, the animal finally passes into a condition of paralysis and general collapse, and within forty-eight hours death ensues from failure of the heart or respiration. The blood is much darkened.

When the effects on the circulation and respiration are studied by means of the kymographion, and the poison is given by the vein in doses of 0.25–0.5 gram, the pulse is at first increased, then decreased, the arterial pressure is lowered, and the respirations are diminished. Repeated doses cause a progressive failure of all three, and death ensues from cardiac or respiratory arrest. The fall of pressure and the alterations in the pulse are due to a direct action on the heart. The cause of the failure of respiration is a direct action on the respiratory centres.

The fatal dose by the stomach is about 0.2 gram per kilo. of body-weight; by the vein, from 0.1–0.2 gram per kilo.

#### *Nitroso- $\beta$ -naphthol.*

In the frog, no special symptoms are developed apart from a general and progressive condition of paralysis of all functions. Shortly after the injection, voluntary movements, respiration, and the heart's action become sluggish; voluntary motion is soon lost; the motor reflexes are weakened and finally abolished. The heart is arrested in diastole and is engorged with blood. The motor and sensory nerves and muscles remain normally irritable after death, but the spinal cord is depressed. The diminution and final loss of reflex excitability are due to the action on the spinal cord.

Given to the dog by the stomach, vomiting occurs within a few minutes, and the drug is ejected before sufficient time has elapsed for much to have been absorbed. Other symptoms observed are quietude, sluggishness in voluntary movements, diminution in reflex excitability, a decrease in the pulse-rate, a primary increase followed by a fall of the bodily temperature, and, generally, an increase in the respiration-rate, although there may be a diminution. If the dose has been sufficient to prove fatal, the animal passes into a condition of general failure of all functions, death resulting from respiratory arrest. The blood is discolored, being very dark, and exhibiting by means of the spectroscope the presence of nitrite of hemoglobin.

When injected into the external jugular vein in doses of 0.12–0.25 gram, there usually occurs a trifling increase in the pulse-rate, which is followed by a diminution, or the pulse may at first be unaffected and then decreased, the pressure is lowered, and the respiratory movements are increased. Repeated doses decrease the pulse-rate and pressure and, finally, depress the



respiratory centres. Although the heart is depressed early in the poisoning and the respiratory centres late, death is always due to a paralysis of the latter.

After section of the pneumogastric nerves the increase in the number of respirations does not occur, showing that the action is on the pulmonary peripheries of these nerves. The decrease late in the poisoning is, however, dependent upon a direct depression of the centres.

The alterations in pulse and pressure are observed just the same after section of the vagi and upper cervical portion of the spinal cord, and must, as a consequence, be due to direct actions on the heart.

The fatal dose when injected subcutaneously is about 0.4 gram per kilo., and is relatively very large, owing to the slowness with which absorption occurs. The minimum fatal dose, injected intravenously, is about 0.04 gram per kilo. It is impossible to determine the exact fatal dose when given by the stomach, because of persistent vomiting.

#### *Nitro-methane.*

No special symptoms are produced in the frog save those attending an increasing condition of depression of all functions: the reflexes are gradually diminished, voluntary motion is lost, the heart's action and respiration become slower and slower, and death ensues. The muscles and sensory nerves are unaffected, but the motor nerves and spinal cord are depressed, especially the latter. The heart is arrested in diastole and is unirritable.

In the dog the hypodermic injection of from one-half to one cc. per kilo. of body-weight will induce death within twenty-four hours. The injection is followed by lassitude, drowsiness, weakness, salivation, urination, defecation and vomiting. The pulse-rate is increased and finally slowed; the temperature is slightly increased during the first hour and then diminished, or it may be decreased from the first; the respirations are variably affected during the early hours, sometimes being unaffected, at other times increased, and at others diminished, but finally are invariably diminished. The motor reflexes gradually weaken, sleep becomes deeper, and, although the animal may be aroused, he immediately relapses; paralysis occurs in the hind extremities, movements cause pain, tremors may be noted, and clonic convulsions occur.

Sleep passes into stupor and then into coma, the respirations fail, and the heart ceases to beat.

Autopsies show that the heart is arrested in diastole, and that the gastro-intestinal mucous membrane is greatly congested and swollen—indicating that death was due to some extent, at least, to this effect.

Special studies made of the actions on the circulation and respiration show that the intravenous injection of about one-half cc. per kilo. always increases the pulse-rate, although this may be preceded by a transient diminution. Even after repeated doses the increase persists and is noted up to the time of death. The arterial pressure is always increased, but this may be preceded by a decline, which is accompanied by a decrease in the pulse, although the latter may be observed without the former. After section of the cardio-inhibitory fibres connecting the corresponding centres with the heart, the same changes in the pulse-rate occur, showing that the action must be either on the heart or accelerator centres. After section both of the vagi and upper cervical portion of the spinal cord, by which the accelerator centres are functionally destroyed, the number of heart-beats is no longer increased as in normal animals. From these facts it is obvious that the increase is due to a stimulation of the accelerator centres. The decrease in the rate which is sometimes observed immediately after the injection and at times just before death is of cardiac origin, because it is noted after the isolation of the heart from the nerve-centres.

The rise of arterial pressure does not occur after section of the upper cervical part of the spinal cord and, therefore, must be due to an action on the vaso-constrictor centres. After very large doses these centres are paralysed.

The respirations are always increased after intravenous injections, and equally well after section of the vagi, proving that this effect is due to a stimulation of the respiratory centres. After several doses this condition gives way to depression, and death occurs from their paralysis long before the circulation shows any appreciable signs of impairment.

The minimum lethal dose is from one-half to one cc. per kilo. of body-weight.

*Nitroso-diethylene.*

Immediately after the injection of this substance into the posterior lymph-sac of the frog the animal's movements become weakened, voluntary motion is lost, the motor reflexes are rapidly diminished and lost, respiratory movements cease, and the heart's action becomes slower and slower and, finally, is arrested. The muscles and sensory nerves retain their normal irritability, but the spinal cord and motor nerves are depressed. The diminution and loss of reflex irritability are due chiefly to the depression of the spinal cord. The heart is arrested in diastole and is unirritable.

In the dog, after the subcutaneous injection of from one-half to one cc. per kilo. of body-weight, there occur salivation, vomiting, lassitude, urination, defecation, weakness, staggering, diminution of reflex activity, occasional howls and whining as though there were paroxysms of pain, dilatation of the pupils, loss of volitional movement, and unconsciousness. The bodily temperature is decreased; the pulse-rate is also lowered, and the respirations gradually fail, although there may be a more or less marked increase at first. Late in the poisoning the vomited matter may be of a distinctly reddish color.

Death occurs from a failure of respiration; the heart is arrested in diastole; and the mucous membrane of the stomach and intestines is swollen and congested.

After the intravenous injection of somewhat smaller doses, and by special studies made of the effects on the pulse and respiration, we have found that the pulse-rate is diminished, the arterial pressure lowered, and the respirations usually at once increased. Should sufficient of the drug be given to be fatal, all three fail, and death occurs from the arrest of respiration.

After section of the pneumogastric nerves we have noted the curious result that, instead of there being a decrease in the pulse-rate, there was always a marked increase—thus indicating that the drug acts simultaneously in opposite ways to affect the rate. The explanation of the causes of these different effects seems apparent in the results which occur in animals in which the accelerator centres are destroyed. Under such circumstances the increase is no longer observed, showing therefore that this effect is due to a stimulation of the accelerator centres. The decrease noted in intact animals appears to be due to a stimulation of the cardio-

inhibitory centres, and the reason why an increase is not manifest is because the effects of the stimulation of these centres are more than sufficient to counterbalance those of the accelerator-centres. Moreover, the action on the former is assisted by another directly on the heart, for it has been found that after the isolation of the heart from the nerve-centres the number of beats is invariably lessened, especially so late in the poisoning. The decrease of pressure is partly due to a depression of the heart and partly to a similar action on the vaso-motor centres and peripheries. The changes in the respiration-rate are due to direct actions on the corresponding centres—first stimulating and then paralysing them.

The minimal fatal dose injected subcutaneously is less than one cc. per kilo. of body-weight; and intravenously, from one-third to one-half cc. per kilo.

#### *Hydroxylamine.*

The injection of hydroxylamine in the case of the frog causes excitement, the animal jumping about more or less continually in a purposeless way; reflex excitability is increased, the slightest touch inducing violent movements; muscular twitchings are present. After awhile all movements are impaired; voluntary motion is lost; there is unconsciousness; the muscles are relaxed, the animal lying sprawled out, although the reflexes are still intact; respiration ceases; the heart's action grows feeble and, finally, stops. The nerves and muscles retain their normal irritability even after death, and the spinal cord seems to be the seat of the reflex disturbances. The heart is arrested in diastole, and the blood is everywhere very dark, almost black.

In the dog, after doses by the stomach of 0.1–0.2 gram per kilo. of body-weight, there occur vomiting, salivation, defecation and urination, weakness, muscular twitchings, convulsive movements of a tonic or clonic character, unconsciousness, an increase in the heart-beats, a diminution of temperature, and sometimes an increase, and at others a decrease, in the respiration-rate. The mouth and gums are distinctly cyanotic. Should the dose be larger and fatal the animal passes into a condition of general paralysis, and death results from a failure of respiration. The blood is everywhere very dark.

Careful studies of the actions on the circulation and respiration by the aid of the kymographion show that when the drug is

injected intravenously in doses of about 0.25 gram the arterial pressure is gradually diminished, although there may occur a slight primary increase; the pulse is usually increased in frequency, and feebler, but the number of beats may be subnormal throughout; the respirations are diminished. We have determined that the alterations in both the pulse and pressure are due to a direct action on the heart, and that the failure of the respirations is the result of a direct depression of the respiratory centres.

The discoloration of the blood is due to the formation of methemoglobin.

The lethal dose by the stomach for the dog is about 0.2-0.3 gram per kilo. of body-weight; and by the vein, 0.06 gram per kilo.

*Aldehyde-ammonia.*

In the frog this substance causes hyper-excitability, restlessness, loss of voluntary motion, diminution of reflex excitability, paralysis, and death. The increase of reflex excitability is due to a direct action on the spinal cord, and the diminution to spinal depression, combined with a depression of both sensory and motor nerves. The muscles do not seem to be affected.

When given to the dog by the stomach, vomiting occurs so readily that the poison is ejected before time has elapsed for any appreciable absorption; but if injected subcutaneously, in the dose of 0.15-0.20 gram per kilo., there is considerable pain induced at the seat of injection, the muscles in the region are decidedly stiffened, and the animal's movements are as though the parts were in splints. This is particularly noticeable if the injection is made in the fleshy portion of one of the legs. The dog is restless, and whines as though in pain; salivation may be present; respiration is increased; the temperature is increased from  $0.2^{\circ}$ - $0.4^{\circ}$  C., and then falls below the normal; the heart-beats are at first increased, but after a time are always less than the normal. Weakness and unconsciousness ensue, attended with a diminution of reflex excitability, and death occurs within 24 hours, the respiration ceasing before the pulse.

When injected into the circulation in doses of 0.25 gram, the arterial pressure, pulse and respiration are increased. The increase of the pulse is usually of a transient character and is soon followed by a diminution; and the respirations are doubled in frequency. After repeated doses—or a single large dose—pressure, pulse and



respiration rapidly fail, and death results primarily from the paralysis of the respiratory centres. By appropriate methods it has been determined that the changes both in pulse and pressure are dependent upon a direct action on the heart, and that the effects on the respirations are the result of a direct action on the corresponding centres. Aldehyde-ammonia is therefore a primary stimulant and secondary depressant to the circulation and respiration; the actions correspond in essential respects with those of the ammonia salts in general.

The lethal dose, subcutaneously injected, is from 0.15–0.20 gram per kilo. of body-weight; and by the vein, about 0.04 gram per kilo.

*Furfurol-sodium Bisulphite.*

The frog, when poisoned by this substance, passes gradually into a condition of paralysis: voluntary motion and reflex activity disappear, the respirations and the pulse become slower and slower and, finally, cease. The sensory nerves are somewhat depressed, but the motor nerves and muscles are apparently unaffected. The loss of reflex activity is due in part to the action on the sensory nerves, but chiefly to a depression of the spinal cord.

It may be given to dogs by the stomach, or subcutaneously, in doses as large as 1 gram per kilo. without inducing other symptoms than a decrease in the pulse, respiration and temperature. The pulse may be reduced within two hours one-third, the respirations one-half, and the temperature from 0.2°–0.8° C. When given by the stomach, vomiting is apt to ensue.

Studies by means of the kymographion show that, when injected into the vein in doses of 1 gram, the arterial pressure, pulse and respiration are diminished. Repeated doses cause further reductions, and death follows from cardiac paralysis. The failure of the pulse is due to a direct cardiac action; the fall of pressure is partly cardiac, but largely the result of a depression of the vaso-motor centres in the medulla oblongata. The respiratory changes are the result of a direct depression of the respiratory centres. Convulsions of a tetanic character were observed in one experiment, just before death.

The lethal dose by the vein is from 0.3–0.5 gram per kilo. of body-weight. 3 grams per kilo., injected subcutaneously, caused the death of a dog within twenty-four hours.

*Oxamic Acid.*

Oxamic acid may be considered inert, since the intravenous injection of 10 grams in divided doses, in the case of a dog weighing 6.5 kilos., did not produce other effects than a slight diminution of arterial pressure and pulse; and, when given by the stomach in similar quantities, or when given to frogs, no apparent results ensue.

*Cyanuric Acid.*

A dog weighing 14 kilos. was given 15 grams of this substance intravenously, without other effects than a slight fall of blood-pressure and a marked increase in the number of respirations.

*Alcohols.*

Investigations made with certain of the alcohols belonging to the ethyl and aromatic series, while too few to permit of a close analysis of their individual physiological differences, enable us to reach valuable generalisations. Among the preparations which we have examined are propylic, iso-propylic, butylic, iso-butylic, heptylic, octylic, allylic, benzylic, and cuminic alcohols. From three to six experiments were performed with each, and these were confined almost solely to observations of the effects on the circulation and respiration, graphic records being made with the aid of the kymographion. In all cases a ten-per cent. solution or emulsion in water was intravenously injected.

From the results of these experiments it may be concluded that the actions of these alcohols are essentially of the same character, but differing in degree. Doubtless more detailed study will elicit some more or less distinctive peculiarities in each preparation.

Ethylic alcohol, which may be taken as a type of the ethyl series, has been carefully studied and its actions on the circulation and respiration may thus be summarised: Small doses increase the frequency and force of the heart-beat, increase the arterial pressure, and increase the respiratory movements. Large doses generally decrease, but sometimes increase, the pulse-rate; primarily increase and then lower arterial pressure, and increase the respirations. Very large doses depress pulse, pressure and respiration. The changes in the heart-beat are due to direct actions on the heart; the increase of pressure is also due to a direct action on the heart. The decrease of pressure is due to a depression both of the heart and vaso-motor apparatus. The primary

increase and final decrease in the respiration-rate are due to a stimulation and subsequent depression of the respiratory centres.

We are led to believe that the actions of the alcohols which we have examined are identical with those of ethyl alcohol, the differences being essentially in degree, and increasing with the acquisition of each radicle; in other words, the higher the alcohol in the series the greater its toxic power. Benzylic and cuminic alcohols belong to the aromatic series, and must to some extent be considered separately, although the actions, qualitatively, are apparently the same as those of the others.

These results are in accord generally with those noted by Dogiel,<sup>1</sup> and Dujardin-Beaumetz and Andigé.<sup>2</sup> Dogiel studied the five lower members of the ethyl series, and found that the actions were the same, and that the toxic power was the least in methylic and greatest in amylic alcohol. The French observers, however, found that methylic alcohol was less poisonous than ethylic alcohol, but that in passing from ethylic to amylic alcohol toxicity regularly increased. Heptylic and octylic alcohols were, when pure, about as toxic as ethylic alcohol, but when diluted with ten times their bulk of absolute alcohol the lethal doses were less than a third.

The minimal lethal doses of the alcohols examined by us when injected intravenously, although likely to be modified by more extended researches, are as follows:

Propylic alcohol,	1.6	-2.5	cc. per kilo. of body-weight.				
Butylic	"	0.3	-0.6	"	"	"	"
Heptylic	"	0.1	-0.12	"	"	"	"
Octylic	"	1.05	-0.1	"	"	"	"
Allylic	"	0.2	-0.24	"	"	"	"
Benzylic	"	0.4	-0.6	"	"	"	"
Cuminic	"	0.25	-0.3	"	"	"	"
Propylic alcohol, (normal),	1.6	-2.5	cc. per kilo. of body-weight.				
"	"	Iso-	1.3-2.	"	"	"	"
Butylic	"	(normal),	0.3-0.6	"	"	"	"
"	"	Iso-	0.6-0.7	"	"	"	"
Butylic alcohol, (primary),	0.3	-0.6	cc. per kilo. of body-weight.				
"	"	(secondary),	1.0-1.5	"	"	"	"
"	"	(tertiary),	1.0-1.2	"	"	"	"

(To be continued.)

<sup>1</sup> Pflüger's Arch. für Physiologie 8, 605.

<sup>2</sup> Compt. rend. 83, 80-82.

ON PARA-XYLENE-DISULPHONIC ACID.<sup>1</sup>

BY JESSE H. HOLMES.

*Introduction.*

The work to be described in this paper was undertaken in the hope of preparing a substance containing two sulphinide groups,  $\text{SO}_2 > \text{NH}$ , in the molecule, the remarkable properties of the simple sulphinide having led to the desire to learn the properties

of a disulphinidé  $\text{C}_6\text{H}_2$   $\left\{ \begin{array}{l} \text{SO}_2 > \text{NH} \\ \text{CO} > \text{NH} \end{array} \right.$ . In order to obtain a sub-

stance of this kind, it seemed simplest to start with para-xylene and make from this a disulphonic acid, as the chances appeared to be in favor of the formation of a di-ortho acid. While a disulphonic acid of para-xylene was prepared without serious difficulty, it was not possible to obtain a disulphinide by the oxidation of its amide, and the constitution of the acid was not determined.

The acid was prepared according to the method used in this laboratory in the preparation of toluene-disulphonic acid,<sup>2</sup> that is, by treating xylene-sulphon-chloride with strong sulphuric acid. The details of the operation were as follows: About 35 grams of pure para-xylene, boiling at  $136^\circ$ – $138^\circ$ , were gradually added, with constant shaking, to about twice the volume of fuming sulphuric acid diluted with a small quantity of ordinary acid. The dilution was found necessary in order to avoid blackening the product; and in spite of it the sulphonic acid obtained was dark-colored. Action took place readily. In the early stages of the operation it was necessary to cool the mixture in water, and at last some warming was required to complete the reaction. After cooling the mixture, a small quantity of water was added, when the sulphonic acid crystallised out:<sup>3</sup> on further dilution it was redissolved. The solution was now diluted to four or five liters, the excess of sulphuric acid precipitated with chalk, the gypsum care-

<sup>1</sup> The work of which an account is given in this paper was undertaken at the suggestion of Professor Remsen and has been carried on under his constant supervision. It gives me pleasure to express here my appreciation of his uniform kindness and consideration.

<sup>2</sup> This Journal **1**, 174.

<sup>3</sup> Ber. d. chem. Ges. **10**, 1009.

fully washed with hot water, and the solution of calcium xylene-sulphonate evaporated to about two liters. The calcium salt was now transformed into the sodium salt by the addition of a slight excess of sodium carbonate, the precipitated calcium carbonate separated by filtration, and the sodium salt solution evaporated to dryness. The sodium salt, after drying, was quite dark-colored. It was treated with an equal weight of phosphorus pentachloride, and then, as the reaction did not seem to be complete, with a considerable excess. It was found later that the yield was very unsatisfactory unless this excess was used, although every precaution was taken to have the salt perfectly dry. The action with the pentachloride took place at once, and after the evolution of hydrochloric acid ceased the semi-liquid mass was heated for some time on a water-bath, to drive off the oxychloride of phosphorus. On adding a large volume of water, xylene-sulphon-chloride separated as a dark, turbid, oily liquid, which did not entirely solidify even when cooled in a freezing-mixture. According to Jacobsen,<sup>1</sup> this chloride, when pure, is a crystalline solid melting at 24°–26°.

The chloride was now treated with four or five times its volume of fuming sulphuric acid. Hydrochloric acid escaped at once, and, on heating, the evolution of this gas continued for some time. The heating was continued until a drop of the mixture showed no turbidity when dropped into water, this being an indication that the acid chloride was completely decomposed. The acids were now diluted and neutralised with calcium carbonate. The sodium salt was prepared as before and was treated with twice its weight of phosphorus pentachloride. After removing the phosphorus oxychloride by evaporation, the disulphon-chloride was separated in several liters of water.

*Xylene-disulphon-chloride*,  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} (\text{SO}_2\text{Cl})_2 \\ (\text{CH}_3)_2 \end{array} \right.$ .—In the impure state, as at first obtained, the disulphon-chloride was a tarry, brownish-yellow mass which adhered strongly to filter-paper, glass, etc. It solidifies easily when cooled in a freezing-mixture. Considerable difficulty was encountered in finding a suitable solvent from which to crystallise it. It dissolves quite readily in cold alcohol, but cannot be obtained again therefrom, probably breaking down to the corresponding disulphonic acid. It is rather easily soluble in benzene, chloroform, acetone, and glacial acetic

<sup>1</sup> Ber. d. chem. Ges. 10, 1009.



acid, but does not crystallise from any of them. When the benzene solution is evaporated to dryness the chloride is left as a transparent, varnish-like cake in the bottom of the beaker, which, on standing, draws together into something like crystalline structure, still containing, of course, all the original impurities. Ordinary benzine, or "petroleum ether," was finally found to be the most satisfactory solvent. The chloride is dissolved in it by boiling in a water-bath, and the solution is allowed to cool very slowly, when the crystals separate in radiating bunches of considerable size.

After a single recrystallisation the chloride was white and appeared to be perfectly pure. The melting-point was  $72^{\circ}$ – $74^{\circ}$ . On standing in contact with the air the crystals turn slightly yellow. The substance was analysed for chlorine by the method of Carius. As preliminary experiments showed it to decompose very easily, the tube was heated only to about  $100^{\circ}$ .—

0.2652 gram of xylene-disulphon-chloride gave 0.2527 gram of silver chloride.

		Calculated.	Found.
$C_8H_8O_4S_2$	232	76.57	...
2Cl	71	23.43	23.56
	<hr/> 303	<hr/> 100.00	

An attempt was made to discover the crystal system and constants, but the planes were found to be so imperfect that the angles could not be accurately measured.

*Xylene-disulphonic Acid*,  $C_6H_2(CH_3)_2(SO_3H)_2$ .—The quantity of chloride prepared as just described was now divided into two parts. The larger portion was transformed into the disulphonamide, which will be spoken of later. The remainder was boiled with water for about twelve hours, in a flask connected with an inverted condenser. At the end of this time a small quantity of organic matter remained undissolved, which was not further affected by boiling water. It dissolved easily when warmed with alcohol, and apparently decomposed. The quantity was too small for any careful investigation.

The solution containing the decomposed chloride was now evaporated to dryness on a water-bath, the residue redissolved, and the evaporation repeated until no more hydrochloric acid was given off. The disulphonic acid was then dissolved again in water, and the solution was treated several times with animal

charcoal, being finally obtained clear with a slight yellow tinge. On evaporation to a small volume the acid crystallises out in needles which are exceedingly soluble in water.

*Barium Xylene-disulphonate*,  $C_6H_2(CH_3)_2(SO_3)_2Ba$ .—A solution of xylene-disulphonic acid was boiled with pure barium carbonate and filtered from the excess of the latter. A perfectly clear, colorless solution was obtained. On evaporation the salt is precipitated in the form of brownish scales which show some signs of crystalline structure under the microscope. It was found impossible to obtain it in good crystals, although it is rather less soluble than the other salts of the same acid. The salt contained no water of crystallisation. Analysis resulted as follows:

I. 0.2825 gram of salt gave 0.1621 gram of barium sulphate.

II. 0.2498 gram of salt gave 0.1443 gram of barium sulphate.

		Calculated.	I. Found.	II.
$C_8H_8O_6S_2$	264	65.84	...	...
Ba	137	34.16	33.74	33.97
	<hr/> 401	<hr/> 100.00		

The analysis as well as the color showed that the substance was not entirely pure.

*Calcium Xylene-disulphonate*,  $C_6H_2(CH_3)_2(SO_3)_2Ca \cdot 4H_2O$ .—The calcium salt was made by neutralising the solution of free acid with finely-powdered Iceland spar. On evaporating to a small volume and allowing to stand, the salt crystallised out in tablets nearly square and with beveled edges. An approximate measurement of their angles indicated that they belonged to the triclinic system, though approaching the symmetry of the tetragonal system. The crystals are biaxial, and are cut by the plane of the optic axes very nearly or quite in the direction of the shorter diagonal.

The calcium salt is very soluble in water, dissolving easily if the solution from which it crystallises be slightly warmed. If the solution is concentrated beyond a certain point the salt is slowly decomposed and fine needle-shaped crystals of gypsum are deposited. One of the four molecules of water of crystallisation could not be driven off without decomposition of the salt. The partially dried salt, which falls apart as a fine powder, is very hygroscopic, taking up water even from calcium chloride in a

desiccator. This property seems to be common to a number of the salts of this acid, so that determinations of water are, at best, only approximate. While standing on the balance-pan, water is absorbed so rapidly as to prevent accurate determinations.

Analysis resulted as follows:

I. 0.3521 gram of the salt lost 0.0524 gram of water at 200° and gave 0.1272 gram of calcium sulphate.

II. 0.2327 gram gave 0.0840 gram of sulphate.

III. 0.1377 gram of salt lost 0.0199 gram of water and gave 0.0500 gram of sulphate.

		Calculated.	I.	Found, II.	III.
$C_8H_8O_6S_2H_2O$	282	75.00	...	...	...
$3H_2O$	54	14.36	14.88	...	14.45
Ca	40	10.64	10.64	10.62	10.64
	376	100.00			

The rest of the salts of xylene-disulphonic acid were made from another stock of material prepared in the same general way, but some slight differences were introduced into the method of preparation, which are noted here because the acid obtained differed in some particulars from that previously made. The chief differences in the process were that the temperature was kept lower in both treatments with sulphuric acid than in the first case, and the transformation from xylene-sulphon-chloride to xylene-disulphonic acid was accomplished by the use of sulphuric acid of specific gravity 1.84 instead of the fuming acid. The blackening of the material was thus avoided and colorless products were obtained throughout the operations. The differences observed between the two products were not very great and may have been due to slight impurities in the first. The two chlorides show the same melting-point—about 72°—but the crystal form of the specimen last prepared was apparently different, the crystals appearing from the benzine solution as thin rectangular plates, instead of showing a prismatic habit as did the first product. The second stock of the acid itself could not be obtained in crystalline form, while the first crystallised in needles. The amide last prepared showed some slight differences, which will be mentioned when the discussion of that substance is reached. The calcium salt, which crystallised well, though not easily, in the first instance, could not be made to crystallise in the second, but sepa-

rated from the solution as an amorphous precipitate on sufficient concentration. The second lot of acid was found to contain a small quantity of sulphuric acid. It was purified by making the lead salt and decomposing its solution by action of hydrogen sulphide.

*Lead Xylene-disulphonate*,  $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{SO}_3)_2\text{Pb} \cdot 3\text{H}_2\text{O}$ .—The lead salt was prepared by dissolving lead carbonate in a dilute solution of the acid. It was found impossible to crystallise the salt, but it was obtained in an amorphous condition by evaporating the solution to small volume. The salt is slightly soluble in alcohol and, when this solution is evaporated nearly to dryness, it crystallises out in long, lustrous but indistinct filaments; so small a quantity goes into solution, however, that this method is not available for purification. As in the case of the crystalline calcium salt, the last molecule of water of crystallisation cannot be driven off without decomposing the compound.

The following results were obtained by analysis:

I. 0.1280 gram gave 0.0096 gram of water and 0.0742 gram of lead sulphate.

II. 0.2485 gram gave 0.1438 gram of lead sulphate.

III. 0.2156 gram lost 0.0154 gram of water.

		Calculated.	I.	Found. II.	III.
$\text{C}_8\text{H}_8\text{O}_6\text{S}_2 \cdot \text{H}_2\text{O}$	282	53.79	...	...	...
$2\text{H}_2\text{O}$	36	6.86	7.50	...	7.14
Pb	206.4	39.35	39.52	39.53	...
	<hr/>	<hr/>			
	524.4	100.00			

*Magnesium Xylene-disulphonate*,  $\text{C}_6\text{H}_2(\text{CH}_3)_2(\text{SO}_3)_2\text{Mg} \cdot 7\text{H}_2\text{O}$ .—This salt was prepared by dissolving magnesium oxide in a solution of the free acid. Like the other salts mentioned, it is very soluble and cannot be crystallised. It was obtained as an amorphous precipitate. As before, the water of crystallisation could not be driven off without decomposing the salt. While it is evident that, calculating the amount of water of crystallisation from the determination of the base alone is not a safe method, yet the results for the latter are so sharp that they are given for what they are worth. The attempt to drive off water was made twice and persevered in until the salt blackened. 18.74 and 18.63 per cent. of water were driven off in these two experiments, while the amount required to correspond with the amount of base present is more than 30 per cent.

I. 0.2904 gram of the salt gave 0.0853 gram of magnesium sulphate.

II. 0.2934 gram lost 0.0550 gram of water and gave 0.0861 gram of magnesium sulphate.

III. 0.1819 gram lost 0.0339 gram of water and gave 0.0525 gram of magnesium sulphate.

		Calculated.	I.	Found. II.	III.
$C_8H_8O_6S_2 \cdot 7H_2O$	390	94.20	...	...	...
Mg	24	5.80	5.87	5.86	5.87

The amounts of magnesium calculated for the weight of the salt after driving off as much water as possible, are as follows :

II. 0.2384 gram of dried salt gave 0.0861 gram of magnesium sulphate.

III. 0.1319 gram of salt gave 0.0535 gram of sulphate.

		Calculated.	II.	Found. III.
$C_8H_8O_6S_2$	264	91.67	...	...
Mg	24	8.33	7.22	7.19
		<hr/>		
		100.00		

*Silver Xylene-disulphonate*,  $C_6H_2(CH_3)_2(SO_3Ag)_2 \cdot H_2O$ .—The silver salt was prepared by dissolving pure silver oxide in a solution of the acid. After several attempts it was obtained in crystalline form as small scales with a pearly lustre. On exposure to light it blackens. Only a very small quantity was made. Analysis resulted as follows :

0.1319 gram of silver salt lost 0.0049 gram of water and yielded 0.0571 gram of silver.

		Calculated.	Found.
$C_8H_8O_6S_2$	264	...	...
$H_2O$	18	3.62	3.71
2Ag	215.3	43.29	43.29
	<hr/>		
	257.3		

Discussion of the probable constitution of xylene-disulphonic acid will be given after the experiments on the oxidation of its amide have been described.

*Xylene-disulphon-amide*,  $C_6H_2(CH_3)_2(SO_2NH_2)_2$ .—As stated above, the main portion of xylene-disulphon-chloride was transformed into the amide. That obtained from the first preparation



will be described first, and the points of difference in the second preparation will be pointed out later.

The chloride, after being dried as completely as possible, was treated with strong ammonia, and the mixture was evaporated to dryness on the water-bath. The chloride turns yellow when first treated with the ammonia, but gradually loses this color and becomes nearly white. It was found better, after some experiments, to pass gaseous ammonia, obtained by warming its concentrated solution, over the dry chloride contained in a flask. The reaction seemed to be complete, though it was thought best to treat the amide so prepared with a small quantity of the ammonia solution before proceeding. After thorough washing with cold water the amide appeared as a fine, light-gray powder. It is very difficultly soluble in water, more easily in a mixture of alcohol and water. It dissolves readily in alkalies, and is reprecipitated by acids as a flocculent white mass. Pyridine dissolves it in large quantities, but deposits it on evaporation or dilution as an amorphous precipitate. It is only slightly soluble in glacial acetic acid, chloroform, and ether. Acetone dissolves it readily, as does also a mixture of acetone with a large proportion of water, but it cannot be crystallised from such a solution. It was finally found best to dissolve the substance in a mixture of about equal parts of alcohol and water, purify by boiling with animal charcoal, boil off most of the alcohol, and crystallise from a large volume of water. On allowing the solution in alcohol and water to cool, the disulphon-amide appears in extremely small, satiny crystals which do not settle even on long standing. When the mixture is stirred the amide in suspension presents a very remarkable appearance, due to the varying reflections from the minute crystal surfaces. The crystals obtained from the solution in water are larger, but are still too small to be distinguished by the naked eye. As seen under the compound microscope, they are found to consist of very thin tabular plates which, in polarised light, show a complicated twinned structure. These plates show parallel extinction, and the characteristic plane angles are  $60^\circ$  and  $30^\circ$ , as nearly as they can be measured on the revolving stage of the microscope. A considerable number of different shapes were observed, the thin plates having three, four and six sides. The crystals appeared to be optically biaxial, but, on account of the extreme thinness of the plates, this could not be certainly determined.

On evaporating the mother-liquors from these crystals, a white flocculent substance was obtained which resembles the amide in some particulars, but settles more readily. A partial analysis indicated that it had the same composition, but was less pure.

An attempt was made to determine the melting-point of the disulphon-amide in a sulphuric-acid bath, but it was found not to melt below the boiling-point of the acid used. It was then determined in an air-bath made by enclosing a small test-tube in a larger one, leaving a considerable layer of air between. This device was found very convenient in determining high melting-points. The disulphon-amide melts with partial decomposition at  $294^{\circ}$ – $295^{\circ}$ .

Analysis of the crystallised substance gave the following results :  
Sulphur, determined by Pearson's method :

I. 0.1882 gram gave 0.3307 gram of barium sulphate.

II. 0.1703 gram gave 0.2988 gram of barium sulphate.

Nitrogen, determined by Kjeldahl's method as modified by Gunning :

I. 0.1778 gram gave 0.0186334 gram nitrogen.

II. 0.3240 gram gave 0.0337456 gram nitrogen.

III. 0.2282 gram gave 0.0248837 gram nitrogen.

Carbon and hydrogen, determined by combustion with lead chromate and lead oxide :<sup>1</sup>

I. 0.2004 gram yielded 0.2687 gram of carbon dioxide and 0.0928 gram of water.

II. 0.1606 gram gave 0.2150 gram of carbon dioxide and 0.0738 gram of water.

		Calculated.	I.	Found. II.	III.
C <sub>8</sub>	96	36.36	36.56	36.50	...
H <sub>12</sub>	12	4.55	5.14	5.12	...
S <sub>2</sub>	64	24.24	24.15	24.02	...
N <sub>2</sub>	28	10.61	10.48	10.41	10.90
O <sub>4</sub>	64	24.24			
	264	100.00			

The disulphon-amide from the second stock of material possessed the same general properties as that from the first, including the melting-point. A sulphur determination after a single crystallisation indicated that it was not entirely pure. After several

<sup>1</sup> Method as modified by R. R. De Roode, This Journal **12**, 220.

recrystallisations some of the crystalline product was obtained, but the larger part resembled the flocculent substance obtained from the mother-liquors of the first crystallised amide. It was not determined whether these differences were due to the presence of an isomeric disulphon-amide or merely to impurities.

The oxidation of the disulphon-amide was next undertaken.—

#### OXIDATION OF PARA-XYLENE-DISULPHON-AMIDE.

In the first experiment a very large excess of both permanganate and alkali was used. The proportions taken were :

Disulphon-amide, . . . . .	5 grams.
Potassium permanganate, . . . . .	40 "
Potassium hydroxide, . . . . .	10 "
Water, . . . . .	1 liter.

These were heated in a water-bath and by the introduction of a current of steam for about four hours. The excess of permanganate was then precipitated by alcohol, the filtrate from the hydroxides of manganese was brought nearly to neutrality by hydrochloric acid and was then evaporated on the water-bath to about 100 cc. On acidifying, after allowing the solution to cool, a considerable precipitation of a fine, crystalline substance occurred. This settled at once and was easily separated. After several recrystallisations it seemed perfectly pure. When heated on platinum foil it left a considerable alkaline residue, which was shown by the flame-test to contain potassium. Nitrogen also was found to be present.

After some further experiments as to the best proportions of reagents, the rest of the amide of the first stock was oxidised, using the proportion of permanganate calculated for the oxidation of the two methyl groups :

Disulphon-amide, . . . . .	20 grams.
Potassium permanganate, . . . . .	48 "
Potassium hydroxide, . . . . .	10 "
Water, . . . . .	2½ liters.

This solution was heated in a water-bath until it was completely decolorised. The filtrate was then concentrated *after* being acidified with hydrochloric acid. On cooling, little rosettes of white crystals appeared and, later, some of the potassium compound mentioned above.

*Disulphamine-para-toluic Acid*,  $C_6H_2(CH_3)(SO_2NH_2)_2COOH \cdot H_2O$ .—The main product was repeatedly crystallised, but could not be obtained in sharp crystals. It comes out always in arborescent radiating filaments. Its melting-point, as determined in an air-jacket, was about  $272^\circ$ . It burns on platinum foil, leaving no residue. Titration with standard ammonia shows it to be a monobasic acid. At  $105^\circ$  it loses one molecule of water of crystallisation. Analysis resulted as follows:

0.1639 gram of the acid lost 0.0095 gram of water at  $105^\circ$ .

$C_8H_{10}O_6S_2N_2$	294	94.23	...
$H_2O$	18	5.77	5.79
	<hr/> 312	<hr/> 100.00	

0.1639 gram of acid on combustion gave 0.0586 gram of water and 0.1835 gram of carbon dioxide.

0.1116 gram gave 0.0094781 gram of nitrogen.

0.1509 gram gave 0.2277 gram of barium sulphate.

		Calculated.	Found.
$C_8$	96	30.77	30.53
$H_{12}$	12	3.85	3.97
$N_2$	28	8.97	8.49
$S_2$	64	20.51	20.72
$O_7$	112	35.90	...
	<hr/> 312	<hr/> 100.00	

It was thought that the potassium salt mentioned above might be the potassium salt of this acid, being precipitated by acids without decomposition in the cold because of its comparative insolubility. A small quantity was boiled with hydrochloric acid, and on cooling an insoluble acid was precipitated, which on recrystallisation resembled the acid oxidation-product, but did not melt at exactly the same point. The percentages of sulphur and nitrogen agree in indicating that the potassium compound is the salt of the acid in question with two molecules of water of crystallisation. At  $150^\circ$  only five-tenths of one per cent. of water was lost; but many substances containing the two sulphamine groups retain their water of crystallisation to a higher temperature. On account of lack of material more attempts to drive off the water were not made. It was supposed when the analyses were made

that all the water was driven off, a constant weight being reached. The analyses resulted as follows :

- I. 0.1938 gram gave 0.0450 gram of potassium sulphate.
- II. 0.1736 gram gave 0.0404 gram of potassium sulphate.
- I. 0.2086 gram gave 0.0165353 gram of nitrogen.
- II. 0.1630 gram gave 0.01240528 gram of nitrogen.

		Calculated.	Found.	
			I.	II.
$C_8H_9O_6S_2 \cdot 2H_2O$	301	81.81	...	...
K	39	10.59	10.41	10.43
N <sub>2</sub>	28	7.60	7.92	7.65

Sulphur determinations varied so widely that they were considered of no value. It is not thought that the evidence as to the composition of this salt is at all conclusive, but it is favorable to the view stated.

*Barium Disulphamine-toluate*,  $C_6H_2(CH_3)(SO_2NH_2)_2CO_2ba \cdot 2\frac{1}{2}H_2O$ .—The barium salt was obtained by dissolving barium carbonate in an aqueous solution of the purified acid. The two samples analysed were made from different preparations of the acid. The salt is exceedingly soluble. It appears from the much concentrated solution in little, warty, spherical masses which are quite hard. These were dried between filters, reduced to fine powder and again pressed between filter-papers. Analysis resulted as follows:

I. 0.1539 gram of salt gave 0.0149 gram of water at 130° and 0.0442 gram of barium sulphate.

II. 0.1810 gram lost 0.0227 gram of water with slight decomposition at 240°, and gave 0.0523 gram of barium sulphate.

		Calculated.	Found.	
			I.	II.
$C_6H_9O_6N_2S_2$	295	72.21	...	...
$2\frac{1}{2}H_2O$	45	11.02	9.68	11.15
Ba $\frac{1}{2}$	68.5	16.77	16.88	16.99
		<hr/>		
		100.00		

The results in this case are not satisfactory, but the composition assigned seems to be justified by the facts. In the second water determination, after the weight was taken, the crucible and salt were left in a desiccator over calcium chloride for the night. The next morning the weight showed that enough water had been



taken up to reduce the percentage removed from 11.15 to 9.45 per cent., which last is about the same quantity that remained when the salt was dried at 130°. On account of the extreme solubility of the salt it could not be purified by recrystallisation, which accounts in part for the inconclusive results as to the basic constituent.

*Calcium Disulphamine-toluate*,  $C_6H_2(CH_3)(SO_2NH_2)_2CO_2Ca$ .—The calcium salt was prepared from finely-powdered Iceland spar. On evaporating the solution to a small volume and allowing it to cool, the whole solidifies to a stiff, transparent, jelly-like mass which could be removed from the beaker as from a mould. No attempt was made to dry it for analysis.

*Lead Disulphamine-toluate*,  $C_6H_2(CH_3)(SO_2NH_2)_2CO_2Pb \cdot 3H_2O$ .—This salt was prepared by dissolving lead carbonate in a solution of the free acid. It crystallises out on cooling the solution in long, lustrous needles which show a tendency to arrange themselves in fan-shaped aggregates. Analysis resulted as follows:

0.1652 gram of the salt lost 0.0203 gram of water and gave 0.0551 gram of lead sulphate. There was a slight yellowing at the end of the water determination, which probably accounts for the high result.

		Calculated.	Found.
$C_6H_5O_6N_2S_2$	295	65.24	...
$3H_2O$	54	11.94	12.28
$Pb_2$	103.2	22.82	22.76
	<hr/>	<hr/>	
	452.2	100.00	

*Silver Disulphamine-toluate*,  $C_6H_2(CH_3)(SO_2NH_2)_2CO_2Ag \cdot 2H_2O$ .—The silver salt was prepared by first making the neutral ammonium salt, an excess of ammonia being added to the acid solution for that purpose. The excess was driven off by evaporation and the silver salt was then precipitated by the addition of silver nitrate. It crystallises on cooling in very fine needles which have a tendency to fan-shaped arrangement, as in case of the lead salt. It is less soluble than the lead salt. A few drops of its solution added to a large volume of cold water render it milky. It decomposes with blackening on exposure to light and air, when in a moist condition. It was dried between filter-papers and analysed with the following results:

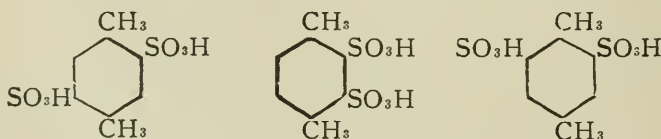
0.1563 gram lost 0.0130 gram of water at  $180^{\circ}$  and gave 0.0386 gram of silver.

		Calculated.	Found.
$C_8H_9O_6N_2S_2$	295	67.20	...
$2H_2O$	36	8.20	8.32
Ag	108	24.60	24.69
	<hr/> 439	<hr/> 100.00	

The products of oxidation of the second preparation of xylene-disulphon-amide showed the presence in small quantity of one substance not observed in the previous experiments. This consisted of crossed and radiating crystals with distinct angles. They were transparent, and differed markedly from disulphamine-toluic acid. The melting-point is about  $274^{\circ}$ . It loses no water on heating to  $105^{\circ}$ . Enough crystals were picked out for a partial analysis, which showed the presence in the compound of 10.35 per cent. of nitrogen and 24.28 per cent. of sulphur. The original disulphon-amide of which this is an oxidation-product contains 10.60 per cent. of nitrogen and 24.24 per cent. of sulphur, but does not at all resemble the substance in question. Sufficient time and material to allow a further investigation were not at my disposal.

#### CONCLUSION.

Plainly, the evidence obtained by the oxidation of xylene-disulphon-amide, as described, is not sufficient to allow any final decision as to the constitution of the disulphonic acid in question. Since, however, in all recorded cases a methyl group and a sulphon-amide group in the ortho-relation yield a sulphinide on oxidation by permanganate, it seems probable that such a relation did not exist between the methyl group oxidised and either of the sulphon-amide groups of the disulphon-amide. There are three possible arrangements of the two sulphonic-acid groups as introduced into the molecule of para-xylene, which may be represented as follows:



In two of these, each methyl group is in the ortho-relation with a sulphonyl-radicle. In the third, however, the two radicles occupy the two ortho-positions with reference to a single methyl group, leaving the other in the meta-position as regards both of them. Between these the evidence does not enable us to decide.

## THE PROTEIDS OR ALBUMINOIDS OF THE OAT-KERNEL.—II.

BY THOMAS B. OSBORNE.

[*Concluded from p. 347.*]

### IV.—PROTEIDS EXTRACTED BY WATER.

The water-extract of freshly-ground oats has a strong acid reaction. The acidity measured by litmus is much less than by phenol-phthalein. 100 cc. of an aqueous extract became neutral to delicate litmus-paper after adding 10 cc. of two-tenths-per cent. potash solution, and 5 cc. more of the same solution were added before phenol-phthalein showed an alkaline reaction. On neutralising the water-extract of oats with two-tenths-per cent. potash, using phenol-phthalein as an indicator, a considerable precipitate appeared, which was soluble in the slightest excess either of alkali or of the acid contained in the extract. This neutralisation-precipitate indicates the presence of so-called *acid-albumin*. The perfectly-neutralised solution when heated to boiling remained clear. On adding 10 per cent. of sodium chloride to the neutralised and filtered liquid, a considerable precipitate formed upon boiling, as well as on the addition of acetic acid. When the unneutralised extract was boiled and the resulting coagulum filtered off, neither sodium chloride nor acetic acid gave a precipitate in the filtrate on boiling. The substance remaining in solution after neutralisation, but precipitated by boiling, in the presence of sodium chloride or on the addition of acetic acid, is a *globulin*, to be described later.

The water-extract, when heated slowly in a test-tube immersed in a beaker of water which in turn was set in a larger beaker of water, showed a turbidity first at 57° C., and minute flocks appeared at 64° C. Heated to 70° and filtered, the solution remained clear until raised to boiling, when a slight precipitate formed. When 10 per cent. of sodium chloride was added to the extract, the turbidity appeared at 44° C., and flocks formed at 64° C.

Five pounds of oats were treated with 6 liters of water for twenty-four hours, pressed out, and extracted a second time for twenty-four hours with the same amount of water. The aqueous

extract reacted strongly acid to litmus, but was not neutralised, as the possible action of the acid was kept in mind, and the immediate object in view was to find what substances were extracted by the use of water alone. The two extracts were united, saturated with commercial ammonium sulphate and the precipitate thereby resulting was filtered off, and scraped from the filter, the paper was washed out with water, the solution being added to the dark olive-green precipitate which partly dissolved to a brown solution. After the solution and suspended precipitate had dialysed for fourteen days in a stream of running water, thymol being added to prevent decomposition, the solution was found to be nearly free from sulphate. The contents of the dialyser were then filtered from a dark-green precipitate which had not dissolved on removing the salts. The filtrate was found not to coagulate on boiling, and was evaporated to dryness on the water-bath, leaving a brown residue which weighed between 1 and 2 grams and gave the following reactions:

With the biuret test it yielded a red-purple color, of a bluer tint than given by peptones or albumose, which increased on standing. Millon's reagent with the aqueous solution gave a strong reaction. Alcohol of 0.9 sp. gr. dissolved a portion which, after removal of the alcohol, was readily soluble in water and reacted for proteids with Millon's reagent and the biuret test. After evaporation of the alcohol on the water-bath, the substance was but partially soluble in water. The alcoholic solution was precipitated by adding stronger alcohol. Fehling's solution gave no reaction until after heating with dilute acid, when a very slight precipitate of cuprous oxide appeared. Very dilute hydrochloric acid gave no precipitate in the solution, and stronger acid made a slight turbidity. These reactions indicate presence of a *proteose* and absence of true *albumin*.

The substance remaining after dialysing the ammonium-sulphate precipitate was treated with 10-per cent. brine of sodium chloride; the resulting solution was filtered off and dialysed till free from chlorides. Nothing precipitated on removal of the salt, the proteid being soluble in water. This fact shows that no globulin had been extracted from the substance which separated on dialysis of the aqueous extract, the globulin having been converted into an insoluble form. This dialysed solution was not coagulated by boiling, and was therefore evaporated to dryness

on the water-bath. The residue, weighing about 1 gram, was not quite completely soluble in water. As much as possible was dissolved in a small amount of water, and filtered from a slight residue. The solution was colored deep yellow-brown, contained a trace of chlorides, gave no precipitate with hydrochloric acid, either very dilute or strong. No biuret reaction was discernible in the colored solution, which gave the proteid coloration with Millon's test, and did not reduce Fehling's solution before treatment with acids. On long standing, after heating with hydrochloric acid, a little cuprous oxide separated. Evidently this substance is the same (*proteose*?) as that obtained from the solution remaining after dialysing the ammonium-sulphate precipitate.

The substance remaining after dialysis and insoluble both in water and in 10-per cent. brine, was found to be partly taken up in  $\frac{1}{2}$ -per cent. sodium carbonate solution, and in dilute hydrochloric acid, being the result of the alteration of globulin, which had passed into solution by means of the salts derived from the oats. The neutralisation-precipitate from sodium carbonate solution was slightly soluble in 10-per cent. brine of sodium chloride. The fact that the ammonium sulphate used in this work was crude and had a slightly acid reaction and a bluish tint, to which the green color of the precipitate was due, may throw doubt on the results here recorded, but as they were mostly corroborated on repeating the trials with pure and neutral ammonium sulphate, I have given them in detail.

The results of a second examination of proteids soluble in water here follow: Five pounds of oats were treated with 7 liters of water for forty-eight hours, thrown on a sieve, the residue pressed out and treated for a short time with 6 liters more of water. The two extracts were united and allowed to settle, when the nearly-clear liquid was syphoned off and saturated with pure ammonium sulphate. After the white precipitate thus produced had stood over night, it separated in large flocks from the liquid, and was filtered out and dissolved mostly in 10-per cent. sodium chloride brine, filtered, and the clear solution dialysed. The precipitate was not completely soluble in 10-per cent. sodium chloride brine nor in water—in these respects resembling the precipitate obtained from the first extract after it had been dialysed. The clear, filtered solution in 10-per cent. sodium chloride brine, on standing, slowly deposited a part of the dissolved substance. The



solution, with the precipitate which had formed, was dialysed until free from salts, and the solution after filtering again was evaporated to dryness on the water-bath, leaving a residue of 1.11 grams. The precipitate filtered out was quite small in amount. The total proteid obtained by saturating with ammonium sulphate was less than that got in the first extraction, probably because the oats were allowed to stand twice as long in contact with water as in the case of the first extract, for it was found that the clear, filtered extract of the ammonium-sulphate precipitate in 10-per cent. sodium chloride brine, on standing, deposited the dissolved substance, so that before the conclusion of the dialysis nearly all the proteid originally soluble in water had lost its solubility.

Weyl states that water converts vegetable globulins into "albuminates," that is, into forms no longer soluble in salt-solutions but soluble in 1-per cent. sodium carbonate solution, or 0.8-per cent. hydrochloric acid, and that a long-continued action of water finally converts the albuminates thus produced into modifications that are no longer soluble in 1-per cent. sodium carbonate solution, or 0.8-per cent. hydrochloric acid. They are then not to be distinguished from "coagulated proteids." This latter change he has observed only for the globulins of peas and oats.

Transformations of this character occurred in the two extracts just described. In the first, after dialysis, the residue insoluble in 10-per cent. sodium chloride brine was partly soluble in  $\frac{1}{2}$ -per cent. sodium carbonate solution, and in the second a body was formed insoluble in water, and in 10-per cent. sodium chloride brine, but soluble in  $\frac{1}{2}$ -per cent. sodium carbonate solution.

To sum up—We have in the aqueous extract of the oat-kernel the following bodies:

1. An *acid-albumin*, precipitated by exact neutralisation of the extract.
2. One or more *globulins*, precipitated from the neutralised extract by sodium chloride and acetic acid; also precipitated by saturation with ammonium sulphate; remaining insoluble in water on dialysis, being, as it would appear, by the action of water, converted into an "albuminate."
3. A *protease*, remaining in solution after dialysis of the ammonium-sulphate precipitate. This body exists also in the dialysed solution of the ammonium-sulphate precipitate from the sodium-chloride extract.

V.—PROTEIDS EXTRACTED BY COLD SODIUM CHLORIDE SOLUTION.

1. *Direct Extraction with Salt-solution*,—Preparations 13 and 14.

Freshly-ground oats extracted with 10-per cent. brine of sodium chloride<sup>1</sup> at 15°–20°, gave a brown solution which, when filtered clear, coagulated as follows: Heated to 42° C., a very slight turbidity formed, which increased very slowly up to 57°, at which temperature it was still slight. Above this point it increased more rapidly, at 61° the solution being opaque, at 72° flocks formed. Heated at 73° some minutes and then filtered, the filtrate became turbid again at 70°, the turbidity increasing somewhat up to 87°; from 87° to 90° the increase was more rapid, but the amount separated at 90° was small. The solution heated to 90° and filtered, became turbid again at 85°, with little change up to 97°. Heated to boiling for a short time and filtered, the filtrate gave an abundant precipitate with acetic acid.

Dilute acetic or hydrochloric acid yields a large precipitate in the brine extract, which is insoluble in a slight excess of the acid. Either saturation with sodium chloride or dilution with water throws down a copious precipitate. The precipitate produced by water, on standing in the dilute salt solution two days, becomes insoluble in 10-per cent. sodium chloride brine and in  $\frac{1}{2}$ -per cent. sodium carbonate solution.

Saturation with ammonium sulphate completely precipitates the proteids from this solution in 10-per cent. sodium chloride brine.

Five pounds of freshly-ground oats were treated twice with 10-per cent. sodium chloride solution, and after filtering, the extract was saturated with commercial—but perfectly neutral—ammonium sulphate, which gave a dark, greenish color to the extracted substances without otherwise affecting their properties. The bulky precipitate was filtered off, suspended in water and dialysed fourteen days, until nearly free from sulphates.

A heavy precipitate remained undissolved. This was filtered out, and the filtrate and precipitate were separately examined.

*Filtrate*.—When heated very slowly in a test-tube, in the manner previously described, the solution was found to become turbid

<sup>1</sup> The sodium chloride employed was the "Diamond Crystal Table Salt," Eureka Salt Company, New York, which is "remarkably free from impurities."

at 58° C.; at 70° C. flocks were formed. Heated to boiling and filtered, the filtrate gave a strong reaction with Millon's reagent. The entire solution was therefore concentrated to a small volume at 40° C., and dialysed until all salts were removed. The coagulation-point of the solution was again taken and found to be the same as before; turbidity at 58° C.; flocks at 73° C. The solution was strongly colored, appearing almost black by reflected light, and by transmitted light a greenish brown. It gave good biuret and Millon's reactions; was not affected by very dilute hydrochloric acid, but was precipitated by stronger acid in the cold. Fehling's solution suffered no reduction, either before or after the action of acid. This solution was then evaporated on a plate below 50° C., and yielded about 6 grams of a very brittle, greenish-black shining substance, very soluble in water, from which alcohol of 0.9 sp. gr. dissolved some proteid.

It is seen that when oats are extracted with 10-per cent. sodium chloride solution, a substance soluble in water and coagulating at 58° to 73° C. is formed, which does not exist in the oats originally, for the aqueous extract, when treated in the same way, yields no substance coagulable even upon boiling.

The amount of this coagulable proteid, which has the properties characteristic of an *albumin*, was too small for analysis (0.5 gram from 2½ kilos. of oats), but its importance in a study of these bodies is great, for Weyl has undertaken to classify the vegetable proteids after the manner now commonly adopted for those of animal origin, and has stated that the extracts of oats and other seeds in 10-per cent. sodium chloride solution coagulate at 55° to 60° C., and consequently contain a *myosin*, since the myosin from animal muscle coagulates under these conditions at this temperature. He also states that besides myosin, *vitellin* exists in these seeds, as shown by filtering out the coagulum formed at 60° C. and heating the solution gradually to 75°, when a second coagulation takes place.

The proteid soluble in salt-solutions, to be described further on, was found, when dissolved in a 10-per cent. sodium chloride solution, to become turbid at 81° C. and to form flocks at 97°. This then has a coagulation-point not far from that of vitellin, but it differs from that substance, in being readily precipitated by sodium chloride even before saturation.

It is seen from the experiments above described that the pres-

ence of a very little coagulable substance may be highly misleading, and gives no certain basis for classifying or identifying the vegetable proteids unless each body is separated from all the others and examined in detail by itself. Weyl did not attempt this except for one preparation from the Brazil nut (*Bertholletia*), and therefore his conclusions based on coagulation-points need further study before they can be accepted.

*Precipitate.*—The precipitate from the dialyser, filtered out of the solution just considered, was treated with 10-per cent. sodium chloride solution. A part of the substance which did not dissolve was filtered out, and the clear filtrate dialysed till free from chlorides, when the proteid was found to be precipitated. This precipitate was filtered out, washed with water, absolute alcohol and ether, and dried over sulphuric acid.

The *globulin* thus obtained, "13," had the following properties:

In 10-per cent. brine of sodium chloride it dissolved readily to a clear solution. Addition of an equal volume of water to this solution produced a copious precipitate. Addition of sodium chloride gave a large precipitate even before saturation. When the solution was diluted till turbid, the turbidity disappeared on warming gently.

Very dilute acetic or hydrochloric acid dissolved the substance readily when salts were not present. The addition of more acid gave no precipitate. Addition of a *very* little sodium chloride to a solution of the substance in very dilute acid, made a slight precipitate; the addition of more sodium chloride threw down an abundant curdy precipitate. The more acid present, the more salt-solution was required to produce a precipitate, and the more salt-solution present, the less the amount of acid required for precipitation.

Dilute solution of citric acid in water (1 : 2000) gave results like acetic acid and dissolved the substance readily to a solution which was *not* coagulated on boiling.

From solution of the substance in 10-per cent. brine, hydrochloric acid throws down a precipitate which is wholly insoluble even in strong solution of sodium carbonate (the filtrate giving no biuret reaction), and is also insoluble in an excess of dilute acid. Acetic acid, on the other hand, gives a precipitate which, at first, is readily soluble in *very* dilute sodium carbonate, but the solution, on standing, becomes turbid.

Hydrochloric acid, in the presence of salt, converts this pro-

teid into a "coagulated proteid"; acetic and citric acids transform it into an "albuminate."

The preparation gave the usual reactions with Millon's reagent, with cupric sulphate and potash, and with nitric acid. The solution in 10-per cent. brine of sodium chloride, on heating became turbid at 81° C., and at 97° C. the formation of flocks occurred. The same solution allowed to stand at summer temperature for more than a month showed no signs of turbidity, decomposition being prevented by adding from time to time a drop of a 20-per cent. alcoholic solution of thymol. The composition of this globulin is here given:

OAT-GLOBULIN.—*First direct Extraction with 10-per cent. Salt-solution—13.*

	I.	II.	III.	I. Ash-free.
Carbon	52.23	52.22	...	52.32
Hydrogen	7.15	6.99	...	7.19
Nitrogen	16.92	17.07	16.90	16.95
Sulphur	0.88	...	...	0.88
Oxygen	...	...	...	22.66
Ash	0.20	...	...	...
				<hr/>
				100.00

*Ash.*—0.7937 gram gave 0.0015 gram ash = 0.20 per cent.

*Carbon and hydrogen, I.*—0.3561 gram gave 0.6822 gram CO<sub>2</sub> = 52.23 per cent. C, and 0.2300 gram H<sub>2</sub>O = 7.15 per cent. H.

*II.*—0.4584 gram gave 0.8778 gram CO<sub>2</sub> = 52.22 per cent. C, and 0.2883 gram H<sub>2</sub>O = 6.99 per cent. H.

*Nitrogen, I* (Dumas method).—0.6225 gram gave 90.85 cc. nitrogen at 18° C. (barometer 765.5 mm. at 22° C.) = 16.92 per cent. N.

*II* (Kjeldahl method).—0.5760 gram gave ammonia = 11.95 cc. HCl (1 cc. = 0.00822 gram N) = 17.07 per cent. N.

*III.*—1.0476 gram gave ammonia = 21.54 cc. HCl = 16.90 per cent. N.

*Sulphur.*—0.8022 gram gave 0.0513 gram BaSO<sub>4</sub> = 0.00705 gram S = 0.88 per cent. S.

A second preparation of globulin was as follows: Five pounds of ground oats were digested with 8 liters of 10-per cent. sodium chloride solution for forty-eight hours, and pressed out. The residue was again subjected to the same treatment. The two



extracts were united, filtered, the clear filtrate saturated with pure ammonium sulphate, and the precipitate thus produced was filtered off. This precipitate was found to be completely soluble in 10-per cent. salt-solution, save a slight turbidity, which was readily cleared up by very dilute sodium carbonate solution. It was therefore removed from the filter, suspended in water, and dialysed for eleven days, whereby the salts were nearly all removed. The precipitate was filtered off, and the filtrate and precipitate were separately examined.

*Filtrate.*—The clear brown filtrate was evaporated to dryness at 50°, leaving an amber-brown, instead of a greenish-black, residue, as was obtained from the first salt-extract.

The properties of this residue agreed exactly with those from the first salt-extract, the difference in color being due to impurities in the ammonium sulphate used in saturating the first extract.

*Precipitate.*—The precipitate in the dialyser was found to remain almost entirely soluble in salt-solution, the trifling residue not taken up by that solvent yielded to dilute sodium carbonate, and, when this solution was neutralised with a slight excess of acetic acid, the separated substance dissolved in solution of common salt.

The dialysed precipitate was therefore filtered, washed by decantation with water, alcohol, ether, and absolute alcohol, and dried over sulphuric acid. This body had all the properties of the one similarly prepared and already described (13). Twenty grams of substance were thus obtained, and by extracting the oat-residue with 10-per cent. sodium chloride solution, until no more proteid was taken up, and proceeding as just detailed, ten grams more of globulin were secured. The yield was accordingly 1.3 per cent. of the air-dried oats. The analyses of this preparation here follow :

OAT-GLOBULIN.—*Second direct Extraction with 10-per cent. Salt-solution—"14."*

	I.	II.	III.	I. Ash-free.
Carbon	52.28	52.33	...	52.37
Hydrogen	7.23	7.17	...	7.24
Nitrogen	16.78	16.90	17.01	16.81
Sulphur	0.89	...	...	0.89
Oxygen	...	...	...	22.69
Ash	0.21	...	...	...
				<hr/>
				100.00

*Ash*.—0.8060 gram gave 0.0017 gram ash = 0.21 per cent.

*Carbon and hydrogen*, I.—0.2894 gram gave 0.5545 gram  $\text{CO}_2$  = 52.28 per cent. C, and 0.1883 gram  $\text{H}_2\text{O}$  = 7.23 per cent. H.

II.—0.2190 gram gave 0.4200 gram  $\text{CO}_2$  = 52.33 per cent. C, and 0.1412 gram  $\text{H}_2\text{O}$  = 7.17 per cent. H.

*Nitrogen*, I (Dumas method).—0.5314 gram gave 77.1 cc. nitrogen at 18° C. (barometer 763.5 mm. at 22° C.) = 16.78 per cent. N.

II (Kjeldahl method).—0.4732 gram gave ammonia = 9.73 cc.  $\text{HCl}$  (1 cc. = 0.00822 gram nitrogen) = 16.90 per cent. N.

III.—0.9973 gram gave ammonia = 20.64 cc.  $\text{HCl}$  = 17.01 per cent. N.

*Sulphur*.—0.8400 gram gave 0.0547 gram  $\text{BaSO}_4$  = 0.007513 gram S = 0.89 per cent. S.

## 2. *Extraction with Salt-solution after treatment with Alcohol,—Preparation "15."*

Since digestion of oats first with water or with salt-solution altered the proteid soluble in alcohol, it was thought possible that by preliminary treatment with alcohol a body might be obtained soluble in salt-solution and yet different from the one extracted directly by that solvent.

To test this hypothesis, three pounds of fine-ground oats were three times extracted, in the cold, with 6 liters of alcohol of 0.9 sp. gr. After pressing out as thoroughly as possible, the residue was treated three times with 10-per cent. sodium chloride solution, the solvent each time being allowed to stand in contact with the oats for twenty-four hours. The first and second extracts were united, filtered, and saturated with sodium chloride. The precipitate was filtered out and found to be but partly soluble in 10-per cent. brine. It was therefore dissolved in solution of sodium carbonate of  $\frac{1}{4}$  per cent., and the filtered liquor was exactly neutralised with acetic acid, which separated the proteid as a white precipitate. After washing thoroughly, by decantation with distilled water, with dilute alcohol, with ether, and finally with absolute alcohol, the substance was dried over sulphuric acid. As it weighed only 2.1 grams, the greater part of the proteid in the oats, soluble in salt-solution, had evidently been converted into an "albuminate."

OAT-GLOBULIN.—*Extracted by 10-per cent. Salt-solution after treatment with Alcohol; dissolved in  $\frac{1}{4}$ -per cent. Sodium Carbonate Solution, and precipitated by Acetic Acid—15.*

		Ash-free.
Carbon	52.39	52.48
Hydrogen	6.93	6.94
Nitrogen	16.82	16.85
Sulphur	0.57	0.57
Oxygen	...	23.16
Ash	0.17	...
		<hr/>
		100.00

*Ash.*—0.3773 gram gave 0.0006 gram ash = 0.17 per cent.

*Carbon and hydrogen.*—0.3187 gram gave 0.6122 gram  $\text{CO}_2$  = 52.39 per cent. C, and 0.1993 gram  $\text{H}_2\text{O}$  = 6.93 per cent. H.

*Nitrogen* (Dumas method).—0.3220 gram gave 47.17 cc. nitrogen at 18° C. (barometer 759.3 mm. at 28° C.) = 16.82 per cent. N.

*Sulphur.*—0.7435 gram gave 0.0304  $\text{BaSO}_4$  = 0.004216 gram S = 0.57 per cent. S.

## VI.—PROTEIDS EXTRACTED BY WEAK POTASH SOLUTION.

### 1. *Extraction after treatment of the Ground Oats with Alcohol,—Preparation 16.*

Another extraction was made in nearly the same manner as that employed by Kreusler in preparing his "Oat-Legumin": Five pounds of freshly-ground oats were treated in the cold with alcohol of 0.9 sp. gr. as long as any proteid was removed. The residue was digested for some time with 7 liters of  $\frac{2}{10}$ -per cent. potash solution. The whole was then thrown on a sieve and the turbid percolate allowed to stand for twenty-four hours.

The dark-colored solution was syphoned off, let stand another day, decanted from the slight sediment, and then precipitated with very dilute acetic acid. After a day the substance had so far settled that about two-thirds of the liquid could be decanted. To the remainder, alcohol was added until the solution had a sp. gr. of 0.93. On further standing, the precipitate deposited and was transferred to a filter. It was washed with stronger alcohol, removed from the paper and dissolved again in  $\frac{2}{10}$ -per cent.

potash solution. A turbid liquid resulted which could not be filtered until a little sodium chloride had been added, which precipitated some of the dissolved proteid. This precipitate was soluble both in additional potash solution and in brine. More salt was therefore added, the nearly-clear solution was then filtered, which process lasted for about a week. Decomposition was entirely prevented by the use of thymol. The filtrate obtained each day was precipitated with dilute acetic acid, the precipitate was washed on a filter with water, then with dilute and afterwards with strong alcohol, and was finally transferred to a flask filled with absolute alcohol. When the filtration was completed and the united precipitates had been digested with absolute alcohol, they were treated with ether and again with absolute alcohol, and lastly dried over sulphuric acid, yielding preparation "16."

OAT-PROTEID.—*Extracted by  $\frac{2}{10}$  per cent. Potash Solution after treatment of the Ground Oats with Alcohol—16.*

	I.	II.	III.	I. Ash-free.
Carbon	52.11	52.18	...	52.45
Hydrogen	6.87	6.74	...	6.92
Nitrogen	16.52	16.48	16.40	16.63
Oxygen	...	...	...	23.19
Sulphur	0.81	...	...	0.81
Ash	0.66	...	...	...
				100.00

*Ash.*—0.7373 gram gave 0.0049 gram ash = 0.66 per cent.

*Carbon and hydrogen, I.*—0.3666 gram gave 0.7005 gram  $\text{CO}_2$  = 52.11 per cent. C, and 0.2265 gram  $\text{H}_2\text{O}$  = 6.87 per cent. H.

*II.*—0.4523 gram gave 0.8651 gram of  $\text{CO}_2$  = 52.18 per cent. C, and 0.2746 gram  $\text{H}_2\text{O}$  = 6.74 per cent. H.

*Nitrogen, I* (Dumas method).—0.3577 gram gave 51.44 cc. nitrogen at 18° C. (barometer 758.7 mm. at 22° C.) = 16.52 per cent. N.

*II* (Kjeldahl method).—0.5037 gram gave ammonia = 10.1 cc.  $\text{HCl}$  (1 cc.  $\text{HCl}$  = 0.00822 gram N) = 16.48 per cent. N.

*III.*—1.0412 gram gave ammonia = 20.77 cc.  $\text{HCl}$  = 16.40 per cent. N.

*Sulphur.*—0.8670 gram gave 0.0510 gram  $\text{BaSO}_4$  = 0.0070 S = 0.81 per cent. S.

For comparison the analyses of the last four preparations are here stated together :

	13.	14.	15.	16.
Carbon	52.32	52.37	52.48	52.45
Hydrogen	7.19	7.24	6.94	6.92
Nitrogen	16.95	16.81	16.85	16.63
Sulphur	0.88	0.89	0.57	0.81
Oxygen	22.66	22.69	23.12	23.19
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

**13** and **14**, extracted directly by 10-per cent. salt-solution.

**15**, extracted by 10-per cent. salt-solution after treating the ground oats with alcohol, then dissolved in  $\frac{1}{4}$ -per cent. sodium carbonate solution and precipitated by acetic acid.

**16**, extracted by  $\frac{2}{10}$ -per cent. potash solution after completely exhausting the ground oats with alcohol.

The four preparations agree in composition so closely that it is fair to assume that they were pure and that the analyses correctly represent the composition of one and the same proteid.

Of the above analyses, **13** and **14** represent the composition of oat-globulin as extracted by 10-per cent. solution of pure sodium chloride and still soluble in that menstruum, while **15** and **16** represent the insoluble or "albuminate" modification of the same proteid.

Analysis of **15** indicates that the globulin is not essentially changed in composition by being dissolved in weak sodium carbonate solution and precipitated therefrom by dilute acid.<sup>1</sup>

Since all proteids, except the coagulated, are soluble in weak alkali, the analysis of **16**, made on a substance extracted by  $\frac{2}{10}$ -per cent. potash solution, may be taken to exhibit the composition of whatever uncoagulated proteids remain in the oat after the direct extraction with weak alcohol. The close agreement of the analysis of **16** with the other analyses leads to the conclusion that the oat-proteids which are not extracted by weak alcohol mainly consist of either the globulin soluble in salt-solution or its "albuminate" modification, or else of a proteid from which these are derived under the influence of the solvents employed in their preparation.

<sup>1</sup> The low figure for sulphur in **15** is accidental, some loss having been incurred in oxidising the substance by fusion with alkali nitrate and carbonate. The determination could not be repeated for lack of material.



The amount of these preparations obtained in a form suitable for analysis was a very small fraction of the total proteid contained in the oats. This was probably due to the conversion of the globulin into an "albuminate" or a "coagulated proteid."

The exact cause of this change has not been ascertained. To test the hypothesis that it might be due to the action of an acid or acid salt contained in the oats, 100 grams of the freshly-ground grain were treated with 800 cc. of  $\frac{2}{10}$ -per cent. potash solution. The resulting mixture was neutral to litmus and did not redden phenolphthalein. Eighty grams of sodium chloride were then added, and the solution, after standing some time, was filtered. Very little proteid was thus extracted. In another trial, 10-per cent. solution of sodium chloride mixed with  $\frac{2}{10}$ -per cent. of sodium carbonate, extracted but a small part of the proteids.

100 grams of oats treated with  $\frac{2}{10}$ -per cent. solution of sodium carbonate gave an extract containing much proteid, which on addition of a little sodium chloride yielded an abundant precipitate. Neutralising the sodium carbonate extract gave a precipitate which was insoluble in sodium chloride solution.

These experiments indicate that the insolubility of the greater part of the oat-proteids in 10-per cent. brine is not due to the presence of an acid or acid salt.

Weyl has stated that when wheat-flour is extracted with sodium chloride solution, the residue yields no gluten on kneading with water, and he considers that the gluten does not pre-exist in the wheat but is a product of ferment action. It was thought that if a ferment occasioned alteration of oat-proteids, its effect might perhaps be prevented by treating the ground oats with a sodium chloride solution heated to 75° C., so that all the soluble proteids coagulable below that temperature would be rendered insoluble and inoperative as ferments. The globulin coagulating at 80° C. ought not to be affected by this treatment. Experiments made to prove this view did not result in the extraction of much if any more globulin than was obtained when a cold salt-solution was employed.

The trials next to be described have an important bearing on the alterations of proteids which take place in the presence of water.

2. *Direct Extraction of the Ground Oats with weak Potash Solution,—Preparation "17."*

100 grams of freshly-ground oats were treated with 500 cc. of  $\frac{2}{10}$ -per cent. potash solution. The mixture, after standing some time, was found to be neutral to litmus-paper. It was then strained through a coarse cloth to remove the husks, and the residue was treated with 100 cc. of  $\frac{2}{10}$ -per cent. potash solution and squeezed out nearly dry. The solutions and washings were united and 100 cc.  $\frac{2}{10}$ -per cent. potash solution added thereto, making 700 cc. in all. The liquid was then faintly alkaline to litmus. On standing, the insoluble matter settled out; the solution was decanted, filtered, and the residue treated again with  $\frac{2}{10}$ -per cent. potash solution. The first potash-extract was very dark brown in color, the second much lighter. A third extract contained very little proteid. The first and second extracts were united, filtered and precipitated with acetic acid added to acid reaction, washed thoroughly with water, alcohol and ether, and dried over sulphuric acid. The preparation weighed 7.8 grams. A portion treated with  $\frac{2}{10}$ -per cent. potash-lye was completely soluble, giving a perfectly clear solution. The rest of the preparation was treated with hot alcohol of 0.9 sp. gr. which took up a little proteid. It was washed with hot alcohol of 0.9 sp. gr. until nothing more was removed, then with absolute alcohol and finally with ether, and was dried over sulphuric acid. After drying at 110° C. the substance was analysed with the following results:

OAT-PROTEID.—*Directly extracted with  $\frac{2}{10}$ -per cent. Potash Solution—17.*

	I.	II.	—Ash-free—	
			I.	II.
Carbon	52.96	...	53.49	...
Hydrogen	6.93	...	7.01	...
Nitrogen	16.23	16.10	16.39	16.26
Sulphur	0.98	...	0.99	...
Oxygen	...	...	22.12	...
Ash	1.00	...	...	...
<hr/>				
			100.00	

Ash.—0.7063 gram, dried at 110°, gave 0.0071 gram of ash = 1.00 per cent.

*Carbon and hydrogen.*—0.2651 gram gave 0.5148 gram  $\text{CO}_2$  = 52.96 per cent. C, and 0.1654 gram  $\text{H}_2\text{O}$  = 6.93 per cent. H.

*Nitrogen, I* (Kjeldahl method).—0.7395 gram gave ammonia = 14.6 cc.  $\text{HCl}$  (1 cc. = 0.00822 gram N) = 16.23 per cent. N.

*II* (Dumas method).—0.4285 gram gave 59.82 cc. nitrogen at  $15^\circ \text{C}$ . (barometer 751.5 mm. at  $21^\circ \text{C}$ .) = 16.10 per cent. N.

*Sulphur.*—0.5196 gram gave 0.0373 gram  $\text{BaSO}_4$  = 0.00512 gram S = 0.98 per cent. S.

### 3. *Extraction of the Ground Oats with weak Potash solution after one hour's treatment with Water,—Preparation "18."*

One hundred grams of ground oats were next treated with 800 cc. of water, the mixture was passed through a cloth to remove husks, and the residue washed with 200 cc. of water. The liquid, with suspended starch, etc., was made up to the volume of a liter, and, after the oats had been for an hour in contact with the water, an equal volume of  $\frac{2}{10}$ -per cent. potash solution was added and intermixed.

After standing over night the strongly-colored solution was decanted from the residue, filtered, precipitated with acetic acid, the precipitate washed with hot alcohol until nothing more could be removed, and then with absolute alcohol and ether, and dried over sulphuric acid. This preparation weighed 4.25 grams. The residue was treated a second time with  $\frac{2}{10}$ -per cent. solution of potash and *very little* more proteid was extracted. After drying at  $110^\circ \text{C}$ . this preparation was analysed with the following results:

*OAT-PROTEID.*—*Extracted by  $\frac{2}{10}$ -per cent. Potash solution after one hour's contact of the Ground Oats with Water—18.*

	I.	II.	I. Ash-free.	II.
Carbon	51.51	...	52.36	...
Hydrogen	7.16	...	7.27	...
Nitrogen	16.95	17.03	17.23	17.31
Sulphur	0.69	...	0.70	
Oxygen	...	...	22.44	
Ash	1.63	...	...	
			<hr/> 100.00	

*Ash*.—0.2760 gram, dried at 110° C., gave 0.0045 gram ash = 1.63 per cent.

*Carbon and hydrogen*.—0.2953 gram gave 0.5576 gram CO<sub>2</sub> = 51.51 per cent. C, and 0.1904 gram H<sub>2</sub>O = 7.16 per cent. H.

*Nitrogen*, I (Kjeldahl method).—0.5867 gram gave ammonia = 12.1 cc. HCl (1 cc. = 0.00822 gram N) = 16.95 per cent. N.

II (Dumas method).—0.5120 gram gave 75.49 cc. N at 15° C. (barometer 753.6 mm. at 23° C.) = 17.03 per cent. N.

*Sulphur*.—0.7210 gram gave 0.0365 gram BaSO<sub>4</sub> = 0.005013 S = 0.69 per cent. S.

In this analysis the fusible ash made the combustion of the last traces of carbon difficult; hence, probably ash and nitrogen are stated a little too high, and the carbon is slightly inaccurate.

#### 4. *Extraction with Potash solution after a day's contact of the Ground Oats with Water,—Preparation "19."*

100 grams of oats were treated in the manner just described, except that instead of the 1000 cc. of potash solution first added, 1000 cc. of distilled water were used. After standing a day, the aqueous solution, which had become clear, was decanted and 1000 cc. of  $\frac{2}{10}$ -per cent. potash solution were added to the residue and let stand upon it over-night. The solution was then decanted from the residue, filtered, precipitated with acetic acid, the precipitate was washed with hot alcohol of 0.9 sp. gr. and with absolute alcohol and ether, and dried over sulphuric acid. The preparation weighed 2.55 grams. The following figures were obtained in its analysis:

OAT-PROTEID.—*Extracted by  $\frac{2}{10}$ -per cent. Potash solution after one day's contact with Water—19.*

		Ash-free.
Carbon	52.29	52.61
Hydrogen	6.88	6.92
Nitrogen	16.89	16.99
Sulphur	0.89	0.89
Oxygen	22.46	22.59
Ash	0.59	...
	<hr/>	<hr/>
	100.00	100.00

*Ash*.—0.5578 gram, dried at 110° C., gave 0.0033 gram ash = 0.59 per cent.

*Carbon and hydrogen.*—0.3300 gram gave 0.6327 gram  $\text{CO}_2$  = 52.29 per cent. C, and 0.2042 gram  $\text{H}_2\text{O}$  = 6.88 per cent. H.

*Nitrogen* (Kjeldahl method).—0.5426 gram gave ammonia = 11.15 cc.  $\text{HCl}$  (1 cc. = 0.00822 gram N) = 16.89 per cent. N.

*Sulphur.*—0.8310 gram gave 0.0543 gram  $\text{BaSO}_4$  = 0.00746 gram S = 0.89 per cent. S.

The three preparations last described were made by extraction with the same dilute potash solution, and under essentially the same conditions in all respects, with the single difference, that while in case of **17** the oats were directly treated with this solvent, **18** was extracted by potash solution after the ground oats had been kept in contact with water for one hour, and **19** after digestion with water for twenty-four hours.

The amount of proteid extracted in the first instance was 7.80 grams.—**17**.

The amount of proteid extracted in the second instance was 4.25 grams.—**18**.

The amount of proteid extracted in the third instance was 2.55 grams.—**19**.

The composition of the three preparations is placed in comparison with that of the oat-globulin **13**, in the subjoined statement.

#### OAT-PROTEID.

	Extracted by—			
	Salt-solution. Direct. <b>13.</b>	Direct. <b>17.</b>	Potash Solution— After contact with water for 1 hour.                      24 hours. <b>18.</b> <b>19.</b>	
Carbon	52.32	53.49	52.36	52.61
Hydrogen	7.19	7.01	7.27	6.92
Nitrogen	16.95	16.39	17.23	16.99
Sulphur	0.88	0.99	0.70	0.89
Oxygen	22.66	22.12	22.44	22.59
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The experiments just detailed tend to show that the action of water upon the crushed oat-kernel induces rapid changes of composition in these proteids simultaneously with their conversion into insoluble modifications.

They also indicate that the *globulin* itself is a result of changes brought about in the presence of water, and is not a body existing as such, ready-formed, in the oats.



5. *Norton's Avenine and Kreusler's Oat-Legumin.*

The substance extracted directly by potash solution without previous exposure of the oats to water, **17**, is probably the same as that which Johnston and Norton originally termed *avenine*, and which the latter obtained by digesting ground oats in water to which a little ammonia was added to prevent souring, as the weather was very warm.<sup>1</sup> The preparation which Norton analysed as *avenine* was, however, extracted by water alone, and was accordingly a mixture.<sup>2</sup> Both Norton and Kreusler applied weak alkali solution to the extraction of proteid bodies from oats *after* the ground grain had been subjected to the action of water.

Norton made and analysed two preparations, accomplishing the extraction by means of dilute ammonia, and threw down the proteid by adding acetic acid to the ammoniacal solution. One preparation, "**A**," was redissolved in strong ammonia at nearly the boiling-point, and again precipitated by acetic acid, then washed (presumably with water), and boiled in alcohol and ether until no more fatty matter was taken up. Another preparation, "**B**," was boiled in alcohol and ether *before* redissolving in very dilute ammonia at 70°–80° C.

Norton made a single analysis of A and two fairly-accordant analyses of B, the average of which is the basis for the corrected analysis given below. He found in both substances 1.00 per cent. of phosphorus, which he includes in the analyses reckoned ash-free. This phosphorus in A nearly equals, and in B exceeds, the ash. If this phosphorus be deducted and the analyses recalculated to a percentage-statement we have the corrected analyses given below. As Norton published no analytical details and used a method of doubtful accuracy (Berthier's) for estimating phosphorus, this correction is perhaps not altogether satisfactory. Norton's nitrogen determinations were all made by Dumas' method. He gives to this substance no special name, but designates it as a "protein body" simply.

Kreusler's preparation of "*Oat-legumin A*" was obtained by suspending 1½ pounds crushed oats in 5 liters of water, adding, to neutralise the acidity, over 3 grams of potassium hydroxide. The mixture stood twelve hours in a cool place, was then thrown on a sieve, the residue washed with water and the liquid left to rest over-night. The turbid liquid was poured off and acidified

<sup>1</sup> Am. J. Sci. [2] 5, 23.

<sup>2</sup> Loc. cit. p. 28.

with acetic acid. The precipitate was washed first with alcohol of 40 per cent., then with that of 80 per cent., then with ether, and lastly was treated with absolute alcohol and dried over sulphuric acid and at 100°. To purify this substance from starch it was dissolved in dilute potash (1 gram to the liter of water), and, from the solution after deposition of all suspended matter, it was thrown down again by acetic acid, washed and dried.

Another preparation, "**B**," was obtained from oats that had been extracted by cold alcohol—and a third, "**C**," from oats exhausted with hot alcohol—previous to treatment with weak potash solution. The analyses of **A** and **C**, corrected by deduction of ash and phosphoric acid, are here tabulated. In his preparation **B**, Kreusler found 16.74 per cent. of nitrogen, but carried the analysis no further.

*PROTEID obtained from Ground Oats after treatment with Water by extracting with weak solution of—*

	<i>Ammonia.</i> (Norton.)		<i>Potash.</i> (Kreusler.)	
	<b>A.</b>	<b>B.</b>	<b>A.</b>	<b>C.</b>
Carbon	53.72	52.35	52.09	51.58
Hydrogen	7.00	6.93	8.03	8.01
Nitrogen	16.94	16.55	16.83	17.61
Sulphur	0.60	1.12	0.96	...
Oxygen	21.74	23.05	22.09	...
	100.00	100.00	100.00	

Norton remarks of his preparation **A** that, dissolving it in hot strong ammonia would seem to have darkened the color and somewhat affected the composition. It will be observed that Norton's **B** does not differ greatly from my analyses **13** and **19**.

Kreusler, doubting the purity of his preparations, boiled them in alcohol of 60 per cent., and finding that something was thereby dissolved, especially from **A**, continued this treatment as long as anything was removed. The dissolved substance contained 16.38 per cent. of nitrogen. The thus "purified" preparations had the following composition, ash-free:

	<b>A.</b>	<b>C.</b>	Average.
Carbon	51.40	51.85	51.63
Hydrogen	7.49	7.49	7.49
Nitrogen	17.29	17.03	17.16
Sulphur	0.85	0.73	0.79
Oxygen	22.97	22.90	22.93
	100.00	100.00	100.00

The average of the last two analyses Kreusler gives as expressing the composition of OAT-LEGUMIN.<sup>1</sup> He observes, in concluding his paper, that the substance, purified by long boiling with alcohol, had almost entirely lost solubility both in potash and acetic acid. It was in fact converted into coagulated proteid; but, that the change of composition was not entirely due to the removal of impurities and in part at least was owing to alteration of the substance itself, must be regarded as almost certain.

It is to be concluded that the "globulin" extracted by 10-per cent. salt-solution, and the "legumin" removed by dilute potash solution after action of water upon the crushed grain, are very similar, perhaps identical in composition, and that neither of them pre-exists in the grain; but the investigation on these points is not altogether conclusive and needs to be continued.

Assuming that Kreusler's analyses are correct, there can be little doubt that his oat-legumin as finally analysed was different from the proteid at first existing in the potash-extract, and was essentially altered in composition as well as in solubility during the processes of preparation and "purification."

#### VII.—PROTEID EXTRACTED BY HOT SODIUM CHLORIDE SOLUTION,—Preparation "20."

Freshly-ground oats were treated with distilled water heated to 65° C., and then sufficient sodium chloride was added to make a 10-per cent. solution. When the addition of salt was begun the liquid had a temperature of 60° C.; when finished, the temperature was 45°. The mixture was digested for about an hour at 45° and a portion of the extract was filtered. The filtrate became turbid immediately on cooling. When gently warmed the turbidity completely disappeared. The perfectly clear solution on further heating coagulated as follows: at 57° C. a very slight turbidity was seen that increased but little up to 78°, whence it rapidly augmented with formation of flocks at 85°.

The remainder of the extract, together with the crushed oats,

<sup>1</sup> In a paper already referred to (Pflüger's Archiv 18, 236), Ritthausen decided that the soda-lime method used by Kreusler was untrustworthy, and stated, as the result of his own analysis by Dumas' method, the nitrogen-content of *Oat-legumin* to be 17.45 per cent. It is now well understood that Dumas' method, carried out as Ritthausen describes in the paper referred to, usually gives too high results, due to retention of air in the oxide of copper, etc., and formation of carbon monoxide during the combustion.—See Report Conn. Station, 1878, p. 111; and 1879, p. 124.

was heated up to  $75^{\circ}$  and filtered as rapidly as possible. A perfectly clear filtrate was obtained which became turbid on cooling. The vessel containing the hot extract was placed in a large water-bath at  $75^{\circ}$  and cooled very slowly. A dense deposit formed which closely adhered to the bottom of the dish, and under the microscope was seen to consist entirely of minute *spheroids* about 0.01 mm. in diameter.

The residual oats, extracted twice again, yielded little more to the hot salt-solution. The proportion of proteid thus obtained was apparently little, if any, greater than that dissolved by sodium chloride solution at  $15^{\circ}$  to  $20^{\circ}$ .

The deposit of spheroids was almost wholly freed from the mother-liquor by simple decantation, and was treated with cold 10-per cent. sodium chloride solution, in which it dissolved very slowly. On warming to about  $40^{\circ}$  the substance melted to a soft, plastic mass, which became softer as the temperature rose, and could be drawn out into glistening threads. At  $65^{\circ}$  the substance became so fluid that the mass broke up and rapidly dissolved to a clear solution.

When a portion of this solution was heated to  $78^{\circ}$  a slight turbidity developed that increased very little up to  $98^{\circ}$ , at which point a few flocks separated. These were filtered out, and the filtrate gave on boiling a considerable coagulum. The filtrate from this coagulum yielded another precipitate on boiling again, and the same result followed these operations to the fourth time. The final filtrate gave with hydrochloric acid a copious precipitate.

This substance was now prepared in greater quantity in the following manner: Five pounds of ground oats were treated with twelve liters of 10-per cent. sodium chloride solution, strained through a hair-sieve to remove the husks, and then heated to  $60^{\circ}$  in a water-bath of  $70^{\circ}$  and maintained at that temperature for an hour. The extract was then filtered as rapidly as possible. The extract, after decanting from a deposit which separated out on cooling, was saturated with pure ammonium sulphate, and the precipitate thus formed was filtered off and added to the deposit formed on cooling. The substance thus obtained was then treated with three liters of 10-per cent. sodium chloride solution heated to  $65^{\circ}$  in a water-bath of  $70^{\circ}$  and filtered as rapidly as possible on a funnel surrounded by hot water. The clear filtrate, which became

turbid at once on cooling, was received in a vessel set in a large water-bath heated to 70°, and the whole was allowed to cool very slowly. When cold the liquid was decanted from the dense deposit that adhered to the bottom and sides of the beaker.

As the substance dissolved to an opalescent solution in distilled water, it was washed with 50-per cent. alcohol as long as with silver nitrate any chlorine was discoverable in the washings; then the washing was continued with absolute alcohol and with ether, and the substance dried over sulphuric acid: 8.5 grams of substance were thus obtained. The salt solution from which the spheroids had deposited was next dialysed, and the proteid which separated out on the removal of the salts was filtered off, washed in succession with dilute alcohol, absolute alcohol, and ether, and dried over sulphuric acid. This preparation weighed 5.64 grams.

The residue of the oats was extracted a second time in the same manner, and the solution was at once saturated with ammonium sulphate. The precipitate thus produced was washed directly with 50-per cent. alcohol, but since the substance dissolved on washing with dilute alcohol as long as much ammonium sulphate remained, the final yield was only 2.6 grams.

The product obtained from the solution of the first ammonium sulphate precipitate in hot brine has the following properties: Under the microscope, before washing, it appears to be perfectly homogeneous and to consist entirely of spheroids about 0.01 mm. in diameter. After washing and drying it forms a dense, snow-white powder. In cold distilled water it dissolves to an opalescent solution which gives a heavy precipitate on the addition of a little sodium chloride; a little more sodium chloride precipitates the aqueous solution almost completely, and on addition of still more salt this precipitate is again dissolved.

Hot distilled water dissolves this proteid completely to a perfectly clear solution from which a considerable part of the substance deposits on cooling.

Dilute acetic acid alone gives no precipitate in the aqueous solution; addition of a little salt together with the acid precipitates it. The precipitate thus produced is soluble in alcohol of 0.9 sp. gr.

When treated with hot dilute alcohol the substance melts and remains suspended in the solution in transparent droplets; addition of either a little salt or a little acetic acid produces no change,



but both together give a clear solution. This solution in alcohol, on cooling, forms a very bulky, transparent jelly. On evaporation, the substance separates as a skin on the surface, which is readily soluble again in dilute alcohol of 0.9 sp. gr.

On analysis the composition of the dried spheroids was found to be as follows:

OAT-PROTEID.—*Extracted by Sodium Chloride Solution*  
at 65° C.—20.

	I.	II.	Ash-free, I.	II.
Carbon	52.13	52.16	52.20	52.24
Hydrogen	6.93	7.02	6.94	7.03
Nitrogen	17.72	17.87	17.75	17.90
Sulphur	0.81	0.73	0.81	0.73
Oxygen	...	...	22.30	22.10
Ash	0.19	...	...	...
			<hr/> 100.00	<hr/> 100.00

*Ash*.—0.4694 gram substance, dried at 110° C., gave 0.0009 gram of ash = 0.19 per cent.

*Carbon and hydrogen*, I.—0.3639 gram dried substance gave 0.6955 gram CO<sub>2</sub> = 52.13 per cent. C, and 0.2270 gram H<sub>2</sub>O = 6.93 per cent. H.

II.—0.4728 gram dried substance gave 0.9036 gram CO<sub>2</sub> = 52.16 per cent. C, and 0.2985 gram H<sub>2</sub>O = 7.02 per cent. H.

*Nitrogen*, I (Kjeldahl method).—0.7768 gram substance gave ammonia = 16.75 cc. HCl Sol. (1 cc. = 0.00822 gram N) = 17.72 per cent. N.

II (Dumas method).—0.4080 gram dried substance gave 62.36 cc. N at 15° C. (barometer 762 mm. at 21° C.) = 17.87 per cent. N.

*Sulphur*, I.—0.7841 gram dried substance gave 0.0463 gram BaSO<sub>4</sub> = 0.0064 gram S = 0.81 per cent. S.

II.—0.8670 gram dried substance gave 0.0460 gram BaSO<sub>4</sub> = 0.0063 gram S = 0.73 per cent. S.

The fact that this substance separated from warm sodium chloride solutions so readily in the form of spheroids, indicated that, under proper conditions, it might be obtained in recognisable crystals. After a very large number of attempts which resulted only in the production of spheroids, a portion of that

substance which had deposited on dialysing the mother-liquor from **20**, was converted into a mixture of spheroids and crystals. The latter were about 0.1 mm. in their greatest diameters and to all appearance had distinct rhombic faces, but they were not perfectly developed and have not since been observed, many efforts to reproduce them having completely failed.

These crystals were obtained by saturating with the globulin a 10-per cent. sodium chloride solution heated to about 60° C., and allowing it to cool slowly in a large bath of warm water.

After many trials with Preparation **20** a portion of it was completely converted into perfectly-formed octahedral crystals which Prof. S. L. Penfield kindly examined and pronounced to be isometric. These crystals were obtained by dissolving some of the substance in cold distilled water and cautiously adding sodium chloride until a copious precipitate resulted. On immersing the test-tube in warm water the precipitate dissolved to a perfectly clear solution. This solution was then allowed to cool slowly in a bath containing about four liters of water heated to 60° C. After a day the deposit was examined under the microscope and found to consist entirely of crystals.

By saturating *distilled water* heated to 60° C. with Preparation **20** and allowing the solution, surrounded by a large volume of warm water, to cool slowly, an abundant deposit of octahedral crystals was obtained, which were, however, not quite so perfectly developed as those just described.

No analysis of these distinct crystals has as yet been made. Their further investigation will be undertaken directly.

#### VIII.—METHODS OF ANALYSIS.

*Drying.*—Preparations preceding **12** were dried in hydrogen at 110° C. to a constant weight. Those following were dried in air at 110° C. Carbon and hydrogen were determined by combustion in a platinum boat in open tube filled with copper oxide and containing in addition a layer of lead chromate and a roll of metallic copper. In the analyses preceding that of **12** the portions taken for each carbon determination were dried separately to a constant weight at 110° C. in a stream of hydrogen, and weighed in a closed tube. For those following, the entire sample was dried to a constant weight in air. By the latter method of drying, slightly higher percentages of hydrogen were obtained when the

substance analysed was in the form of a light hygroscopic powder; the dense preparations obtained from alkaline solutions, not being so hygroscopic, gave slightly lower percentages of hydrogen: the difference is attributable to moisture unavoidably absorbed by the dry, light powder during weighing and transferring to the combustion-tube, the analyses being made in very damp summer weather.

The accuracy of the determinations was repeatedly controlled by analyses made on pure sugar.

*Nitrogen.*—Nitrogen determinations were made by both the Kjeldahl and Dumas methods, in the manner customary in the Station Laboratory.<sup>1</sup> Preceding 12 the determinations were made upon the substance dried over sulphuric acid, a correction being applied for the moisture contained in the sample as found by drying it at 110° C. Subsequent determinations were made on the fully-dried sample.

*Sulphur.*—Sulphur was determined by fusion with sodium hydroxide and potassium nitrate, dissolving the fused mass in water, neutralising the alkali with a considerable excess of hydrochloric acid, evaporating to dryness to decompose nitrates and to remove excess of acid, dissolving the dry residue in six or seven hundred centimeters of water, allowing the solution to stand for twenty-four hours, filtering, heating to boiling, and precipitating with 3 cc. of a 10-per cent. solution of barium chloride.

In the analyses of 8, evaporation to dryness was omitted, the barium sulphate being fused with sodium carbonate and reprecipitated. In all cases the ash of the preparations was carefully examined for sulphates, but none was found in any instance.

Blank experiments with the reagents proved them to be entirely free from sulphur.

*Ash.*—Ash was determined by combustion in a platinum crucible, no difficulty being experienced in burning any of the preparations except 18.

## IX.—SUMMARY OF RESULTS.<sup>2</sup>

1. The proteid body removed from freshly-ground oats by direct extraction with weak alcohol—first observed by Norton and

<sup>1</sup> Annual report Conn. Station, 1879, p. 124; and This Journal 2, 27.

<sup>2</sup> This summary is a revision of a part of Bulletin 105, issued by the Connecticut Agricultural Experiment Station, December, 1890, which contained some minor errors that are here corrected.

by him designated *glutin*—when dehydrated by absolute alcohol and dried over sulphuric acid, is a light yellowish powder, insoluble in pure water as well as in absolute alcohol, soluble in mixtures of alcohol and water, soluble also in dilute acids and alkalies, and from these solutions thrown down by neutralisation. Separated from its solution in alcohol of 60 per cent. by evaporating off the alcohol, it forms a yellowish, slimy mass. Its composition (as found for preparation 8<sup>1</sup>) is given in the table, p. 338, under **I**. This substance is remarkable for its considerable content of sulphur, which is exceeded by that of keratin alone among the proteids, and is otherwise equaled only by that recorded in some analyses of serum-albumin. See p. 340.

2. When the substance described above is heated with dilute alcohol for some time, it coagulates and become insoluble in that liquid, but without apparent change of composition. **II** (p. 338) is the average of three accordant analyses of this coagulated form of the proteid, which is soluble in alcohol, made on preparations 7, 4 **A** and 4 **B** (pp. 334-336).

Kreusler obtained this material from the oat, but what Ritt-hausen and he named *oat-gliadin* was a product of its further alteration by the chemical treatment to which it was subjected with a view to purification. (See pp. 340-341.)

3. When oats are first treated with water or 10-per cent. solution of common salt, before extraction with dilute alcohol, the proteid, soluble in alcohol, undergoes alteration, and a body of different composition and properties results. In the table, **III**, is the mean of closely-agreeing analyses of this substance made on preparations 9, 10, 11 and 12; it is much more soluble in dilute alcohol than **I**, and is not coagulated or transformed into an insoluble modification. When wet with absolute alcohol, the moisture attracted from the air shortly renders it gummy and tenaciously adhesive, unlike **I**.

Its composition, as regards carbon, hydrogen, and nitrogen, is very near to that found by Dumas and Cahours, and also by v. Bibra, for *gliadin* or *plant-gelatin* (extracted by hot alcohol from wheat-gluten and remaining dissolved in the alcohol when cold).

4. The chief proteid extracted by cold 10-per cent. salt-solution behaves towards reagents like the *myosin-glubolin* from animal muscle, as first stated by Weyl. Contrary to Weyl's observations,

<sup>1</sup> Vide p. 338.

however, the coagulation-temperature ( $80^{\circ}$ – $100^{\circ}$ ) is much higher than that of animal myosin ( $55^{\circ}$ – $60^{\circ}$ ). This proteid appears to be the result of a transformation similar to that by which myosin is formed from myosinogen. Its composition—the average of several analyses on preparations **13** and **14**—is given under **IV**, and is very near to that of muscle myosin. The greatest proportion of this proteid extracted by salt-solution from the oat was 1.3 per cent. (See pp. 389–394.)

5. The proteid extracted, after complete exhaustion of the oats with alcohol of 0.9 sp. gr., by 10-per cent. salt-solution (analysis of Preparation **15** under **V**), and that dissolved out by dilute potash (analysis of Preparation **16** under **V a**), have so nearly the same composition as the globulin extracted by salt-solution directly, that they may be regarded as originally identical, **IV** representing the soluble form, **V** and **V a** the insoluble or “albuminate” modification. (See pp. 394–399.)

6. When ground oats are directly extracted by weak potash solution, without previous treatment with water or dilute alcohol, nearly the whole of the proteids is dissolved. The substance so extracted, after completely removing the body soluble in weak alcohol, is perhaps the same as that first designated *avenine* by Johnston and Norton, who extracted oats with dilute ammonia-water. Its composition, as indicated by analysis of a single preparation, **17**, is stated under **VI**. (See also pp. 399–400 and 403.)

7. When ground oats are exposed to the action of water, a large share of the proteids becomes insoluble in dilute potash solution, the amount so rendered insoluble increasing with the duration of the contact with water. One hour's treatment with water rendered one-half, twenty-four hours' treatment made two-thirds insoluble in  $\frac{2}{10}$ -per cent. solution of potash. The composition of the part soluble in potash, after action of water (and removal of the alcohol-soluble proteid), as found in analyses of Preparations **18** and **19**, the average of which is stated under **VII**, is the same as that of the globulin soluble in salt solution, **IV**. This proteid, obtained by extraction with potash, *after* the action of water, is probably the substance which Kreusler converted into his *Oat-Legumin* by the “purifying” process to which he subjected it. It is also the “protein body” which Norton extracted by weak ammonia and analysed. (See pp. 400–405.)



8. When ground oats are extracted with 10-per cent. sodium chloride solution heated at 65° C., a proteid separates on cooling, in the form of spheroids. This substance differs in composition and properties from that obtained by cold salt-extraction, as well as from all proteids hitherto described. It is soluble in pure water, precipitated from such solutions by a little sodium chloride, is again dissolved by a certain additional quantity, and is precipitated completely by saturation with this salt. In the presence of a little sodium chloride and acetic acid it is soluble in alcohol of 0.9 sp. gr. From solutions in distilled water, as well as from those in sodium-chloride brine, it has been obtained crystallised in regular octahedra. Analysis (of spheroids) under VIII. (See pp. 405-409.)

9. The aqueous extract of ground oats was found, in agreement with Norton and Kreusler, to contain very little proteid substance. The proteids thus dissolved appear to be, first, an *acid-albumin*; second, a *globulin* or *globulins* similar in reactions to that extracted by 10-per cent salt-solution, and third, a *proteose*. No true albumin was found in the water-extract. (See pp. 385-389.)

10. In the salt-extract a very small amount of a body was found, having the reactions of *albumin*, but not analysed (pp. 389-390).

# X.—TABLE OF COMPOSITION OF PROTEIDS FROM THE OAT-KERNEL.

	I.	II. <sup>1</sup>	III. <sup>1</sup>	IV.	V.	V a.	VI.	VII. <sup>1</sup>	VIII.
Carbon,	53.06	53.10	53.70	52.34	52.48	52.45	53.49	52.49	52.22
Hydrogen,	6.94	6.91	7.00	7.21	6.94	6.92	7.01	7.10	6.98
Nitrogen,	16.38	16.49	15.71	16.88	16.85	16.63	16.39	17.11	17.85
Sulphur,	2.26	23.50	1.76	0.88	0.57	0.81	0.99	0.80	0.77
Oxygen,	21.38		21.83	22.69	23.16	23.19	22.12	22.50	22.18
			<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

The numbers over the analyses in the above table correspond with those of the paragraphs in the foregoing summary.

LABORATORY OF THE CONN. AGRICULTURAL EXPERIMENT STATION.

<sup>1</sup>Average of several analyses.

## THE DECOMPOSITION OF CHROMITE BY THE ELECTRIC CURRENT.

BY EDGAR F. SMITH.

Two years ago I mentioned<sup>1</sup> that if finely divided chromite were suspended in melted alkali, and an electric current allowed to act upon the mixture, the mineral would undergo decomposition, its chromic oxide being changed to a soluble alkaline chromate. Details of the experiments made at that time were not published, because difficulties were encountered which necessitated a more careful study of the subject.

The early trials were made with a current of one ampère. The oxidation of the mineral was apparently finished in fifteen minutes, but the desire to reduce the time-factor, by increasing the strength of the acting current, led me astray. Many successful and unsuccessful decompositions were made before conditions were found which gave satisfactory results. Among other things it was observed that by using a strong current the latter seemed to act chiefly upon the iron oxide and the caustic alkali, liberating larger or smaller quantities of the metal from each. After the decomposition of the mineral had proceeded to a certain extent, the action just mentioned seemed to commence, and undecomposed chromite always remained. Without describing the various modifications that were tried in the hope of attaining success, I will briefly outline the method which finally gave, and has continued to give, good results.

*Method of Oxidation.*—Melt 30–40 grams of stick potash in a nickel crucible,  $1\frac{7}{8}$  inches high and 2 inches wide; heat gently until the excess of moisture has been expelled. The crucible is then placed upon a heavy copper-wire ring, attached to the anode of a storage-cell.<sup>2</sup> A small flame is held under the crucible during the entire decomposition. The weighed mineral is carefully brushed from a watch-crystal upon the liquid alkali, the crucible covered with a perforated glass, and the platinum rod, attached to the cathode of the battery, lowered into the melted mass. Set the current in operation; particles of the melted material are thrown

<sup>1</sup> J. Franklin Inst., April, 1889; Ber. d. chem. Ges., 22, 1019.

<sup>2</sup> A picture of the apparatus arranged for a decomposition of this kind is given in Ber. d. chem. Ges., 23, 2276; J. Franklin Inst., 130, 145; and in the writer's "Electrochemical Analysis," p. 111.

against the under-side of the cover-glass, but the liquid soon collects in drops and falls back into the crucible, thus returning any traces of ore that at first may have been projected from the crucible by the bursting of the gas-bubbles.

Experience has demonstrated that it is best to make the crucible the anode; but before finally interrupting the current, the latter should be reversed by means of a commutator, which, together with an ampèremeter, is always in circuit. The current is reversed for this reason: metallic iron is deposited upon the cathode and may enclose particles of the ore, removing them from the oxidising field. By reversing the current the imprisoned material is set free and exposed to oxidation.

The quantity of mineral taken for a determination may vary from 0.1-0.5 gram. It should be quite fine, although it was never as finely divided as seemed necessary for complete decomposition by other methods. The current employed in the oxidation of the material *should not exceed one ampère* for the quantities given above. As to the time required for the decomposition, it can only be said that while the greater part of the mineral is unquestionably decomposed in fifteen minutes, it is best to let the current act for a period of thirty to forty minutes. Much depends upon how refractory the sample under analysis may prove to be. Chromites vary in this respect. It is a difficulty with which all methods must contend. Hence, at least one half-hour should be allowed for an oxidation by the electrolytic method. As the decomposition advances the melted alkali acquires a yellow color. The portion that creeps to the edge of the crucible and about the cover-glass has the appearance of cauliflower.

The current can now be interrupted. Raise the platinum rod (the cathode) from the liquid, remove the cover-glass carefully from the crucible with a nickel tongs, rinse its under-surface with water, collecting the latter in a beaker. The crucible is lifted from the ring supporting it and allowed to cool. The platinum cathode should be rinsed with water. It will show a black appearance, due to the metallic iron that had been deposited upon it. It is my plan to dissolve off the iron with dilute hydrochloric acid, to assure myself that undecomposed ore was not present.

When the nickel crucible is cold, place it in a beaker of 300 cc. capacity, cover with water, and digest upon a warm iron plate.

In a few minutes the contents of the crucible can be entirely removed. The liquid now contains the excess of alkali, sodium aluminate, silicate, manganate, chromate, etc. After digesting for some time upon a warm iron plate, filter off the insoluble portion and thoroughly wash it with boiling water. The yellow alkaline solution is now ready for the determination of the chromium.

Treat the residue with warm hydrochloric acid. It should dissolve. It may happen that when quartz is present in the ore there will be a slight residue, but this is immaterial, provided it is not dark in color. In the analyses given later, the oxides remaining after treating the fused mass with water *dissolved completely* in warm hydrochloric acid.

*Chromium Determination.*—This may be made either gravimetrically or volumetrically. In the later determinations I used the volumetric method almost exclusively. To this end the chromate solution was acidulated with sulphuric acid, and a weighed portion of ferrous sulphate added, the excess being determined with a standardised bichromate solution. Potassium ferricyanide served as an indicator. In several instances the excess of ferrous salt was determined with potassium permanganate. This course, however, was abandoned, as I failed to read the end-reaction with sufficient accuracy. By using the volumetric method, I believe it possible for the analyst to decompose a chrome ore and determine the chromium content within the space of an hour. Several crucibles can be connected up in the same circuit, and a series of determinations made quite rapidly and with as much accuracy as by any one of our present methods.

### Results.

1. 0.1080 gram chromite gave 51.77 per cent.  $\text{Cr}_2\text{O}_3$ .
2. 0.4787 gram chromite gave 51.55 per cent.  $\text{Cr}_2\text{O}_3$ .
3. 0.2729 gram chromite gave 51.23 per cent.  $\text{Cr}_2\text{O}_3$ .
4. 0.1085 gram chromite gave 51.74 per cent.  $\text{Cr}_2\text{O}_3$ .
5. 0.4184 gram chromite gave 52.02 per cent.  $\text{Cr}_2\text{O}_3$ .

By the Dittmar method of decomposition a sample of the same ore gave 51.70 per cent.  $\text{Cr}_2\text{O}_3$ .

A second chromite, decomposed by the current, gave as follows :

6. 0.1515 gram chromite gave 48.01 per cent.  $\text{Cr}_2\text{O}_3$ .
7. 0.2029 gram chromite gave 48.34 per cent.  $\text{Cr}_2\text{O}_3$ .

8. 0.3174 gram chromite gave 48.21 per cent.  $\text{Cr}_2\text{O}_3$ .

9. 0.2071 gram chromite gave 48.38 per cent.  $\text{Cr}_2\text{O}_3$ .

A portion of the ore oxidised by the Genth method and the chromic oxide determined gravimetrically gave 48.50 per cent.  $\text{Cr}_2\text{O}_3$ .

A light-colored chromite powder gave the following results:

10. 0.2012 gram chromite gave 32.00 per cent.  $\text{Cr}_2\text{O}_3$ .

11. 0.2130 gram chromite gave 31.50 per cent.  $\text{Cr}_2\text{O}_3$ .

A gravimetric determination of the chromium, after decomposition by the method of Dr. Genth, gave 31.90 per cent.  $\text{Cr}_2\text{O}_3$ .

A fourth specimen of chromite showed the following percentage of chromic oxide, after decomposition by the current:

12. 0.2295 gram chromite gave 42.20 per cent.  $\text{Cr}_2\text{O}_3$ .

13. 0.2225 gram chromite gave 41.70 per cent.  $\text{Cr}_2\text{O}_3$ .

By the Genth method this ore gave 41.30 per cent.  $\text{Cr}_2\text{O}_3$ , while 41.98 per cent.  $\text{Cr}_2\text{O}_3$  was found after a decomposition made by the Dittmar method.

The writer would here acknowledge his indebtedness to Mr. D. C. Wallace for the care and skill with which he conducted the many oxidations that were considered desirable before publishing the facts contained in this communication.

CHEMICAL LABORATORY, UNIVERSITY OF PENNSYLVANIA.

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## ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND FRANK MUHR.

Having found after many trials that gold could be completely precipitated by the current from solutions of potassio-auric cyanide, steps were taken to ascertain from what metals it could be separated. Former studies<sup>1</sup> showed that a current of one-hundredth ampère did not precipitate palladium from a solution containing an excess of potassium cyanide until after it had acted for a period of thirty-six hours. This behavior pointed to a possible separation of gold from palladium. These two metals were,

<sup>1</sup> This Journal 12, 252.



therefore, experimented upon with the current, under the conditions indicated in the following table :

	Gold present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Palladium present. Gram.	Gold found. Gram.	Difference in percentage from theory.
1.	0.1162	1.50	150 cc.	0.80 cc.	0.1200	0.1162	..
2.	"	"	"	"	"	0.1163	+ 0.08
3.	"	"	"	"	"	0.1162	..
4.	"	"	"	"	"	0.1163	+ 0.08
5.	"	"	"	0.40 cc.	"	0.1160	- 0.17
6.	"	"	"	"	"	0.1156	- 0.52
7.	"	"	"	1.00 cc.	"	0.1164	+ 0.17
8.	"	"	"	"	"	0.1158	- 0.34

The time allowed for the precipitation of the gold varied from twelve to fourteen hours. Cold and hot water were used for washing the precipitated metal. The deposits were made directly upon the platinum dishes. The gold was subsequently dissolved off by placing dilute potassium cyanide in the vessels and then connecting the latter with the anode of a feeble Crow-foot battery.<sup>1</sup> The gold cyanide solution was decomposed with *aqua regia* and, after obtaining gold chloride, this was carefully examined for palladium. None was discovered.

*Gold from Copper.*—The previous electrolytic separation of silver from copper<sup>2</sup> indicated that gold might perhaps be separated with equal facility from the latter metal, inasmuch as the complete deposition of the gold did not require a current much stronger than that necessary for the precipitation of silver. The separation proved successful under the conditions given below :

	Gold present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Copper present. Gram.	Gold found. Gram.	Difference in percentage from theory.
9.	0.1725	1.5	150 cc.	0.8 cc.	0.1250	0.1725	..
10.	0.1725	3.5	"	0.4 cc.	"	0.1728	+ 0.17
11.	"	"	"	"	"	0.1720	- 0.29
12.	"	"	"	"	"	0.1735	+ 0.50
13.	"	3	"	0.8 cc.	"	0.1736	+ 0.60

Copper was not detected in the precipitated gold. The time required for the precipitation, washing and drying of the deposits was the same as in the separation of gold from palladium.

*Gold from Cobalt.*—In the electrolytic separation of mercury

<sup>1</sup> J. Franklin Inst. **131**, 300; J. Anal. Chem. **5**, 205.

<sup>2</sup> J. Franklin Inst. **129**, 241.

from cobalt, and of silver from cobalt,<sup>1</sup> satisfactory results were obtained only after the quantity of alkaline cyanide present had been reduced to 3 grams. This quantity was used in the following separations, although its increase was not accompanied by the difficulties attending the separation of the metals to which reference has just been made. Indeed, in this particular case no special effort was required in order to get satisfactory results.

	Gold present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Cobalt present. Gram.	Gold found. Gram.	Difference in percentage from theory.
14.	0.1792	3	150 cc.	0.6 cc.	0.15-0.20	0.1789	-0.11
15.	"	"	"	"	"	0.1799	+0.49
16.	"	"	"	"	"	0.1794	+0.11
17.	"	"	"	"	"	0.1799	+0.49

The current acted upon the double cyanides through the night.

*Gold from Nickel.*—This separation can be made without difficulty, as is proved by the four trials given below.

	Gold present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Nickel present. Gram.	Gold found. Gram.	Difference in percentage from theory.
18.	0.1725	2½	150 cc.	0.5 cc.	0.1373	0.1724	-0.05
19.	0.1725	3	"	1.0 cc.	"	0.1718	-0.49
20.	0.1467	2½	"	0.5 cc.	"	0.1462	-0.34
21.	"	"	"	"	"	0.1460	-0.48

The electrolytic separation of mercury from zinc in cyanide solution, as well as cadmium and silver from the latter metal, occurred without any special difficulty.

*Gold from Zinc.*—The current to decompose the double cyanide of zinc and potassium must yield at least 2-3 cc. electrolytic gas per minute, so that special precautions in regard to the following separation need not be given:

	Gold present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Zinc present. Gram.	Gold found. Gram.	Difference in percentage from theory.
22.	0.1792	3	150 cc.	0.5 cc.	0.2000	0.1796	+0.22
23.	"	"	"	0.6 cc.	"	0.1797	+0.27
24.	"	"	"	"	"	0.1790	-0.11
25.	"	"	"	"	"	0.1798	-0.33

It will be noticed in the preceding experiments that the gold is either slightly in excess or below the theoretical amount. This cannot be due to incomplete precipitation or to the co-precipitation of the other metal present in the double cyanide solution, for

<sup>1</sup> J. Franklin Inst. 129, 239, 244.

in each of the preceding cases careful search was made for all the metals operated upon; the variations from the theoretical requirements must therefore be attributed to some other cause. The precipitations were made in platinum dishes; these varied in weight from 60–71 grams. Care was not taken to weigh at any particular period of the day, nor were the precipitating-vessels allowed any definite time for drying, etc.

The battery used to precipitate the gold consisted of 6–10 Crowfoot cells. The poles, during precipitation, were  $1\frac{1}{2}$  inches apart. Cover-glasses were placed over the electrolysed solution to prevent loss and to exclude dust. The latter can easily cause the metal precipitated to collect in little spongy masses, which are readily detached upon washing. To determine when the gold was fully precipitated, the level of the liquid in the dish was raised by the addition of distilled water. Before the current was finally interrupted the poles were brought more closely together, and the electrolytic action continued for a half-hour longer. It is better to do this than to remove a portion of the liquid and apply some special test to it.

It is scarcely necessary to add that if the clean platinum surface remains uncoated, the precipitation of metal is finished.

The current of the strength given in the preceding experiments *does not precipitate* platinum either from hot or from cold solution of its double cyanide when an excess of alkali cyanide is present. In this respect platinum resembles palladium. This behavior prompted us to attempt, with good results, the separations recorded in the following lines:

#### *Gold from Platinum.*

	Gold present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Platinum present. Gram.	Gold found. Gram.	Difference in percentage from theory.
26.	0.1467	$2\frac{1}{2}$	150 cc.	1 cc.	0.2433	0.1474	+ 0.48
27.	"	"	"	"	"	0.1474	"
28.	"	"	"	"	"	0.1468	+ 0.05
29.	"	"	"	"	"	0.1461	— 0.40

*Silver from Platinum.*—In the first trials of the separation of gold from platinum the dishes were coated with a thick layer of metallic silver. When the platinum double cyanide solution was electrolysed, platinum metal was deposited upon the silver. Its precipitation was, however, incomplete; furthermore, silver

passed into solution. This behavior seemed to us to promise little in the way of separating silver from platinum. However, after dissolving definite amounts of salts of the two metals and adding an excess of potassium cyanide, the solution was directly electrolysed, when the silver separated upon the dish, perfectly free from platinum. Currents of greater strength than that given in the recorded experiments will throw out traces of platinum. It shows itself in dark spots, distributed over the white silver surface. In such cases a black, though minute, residue will always be noticed when the precipitated silver is dissolved in dilute nitric acid. The results were as follows:

	Silver present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Platinum present. Gram.	Silver found. Gram.	Difference in percentage from theory.
30.	0.0770	2½	150 cc.	1 cc.	0.2433	0.0772	+ 0.25
31.	"	"	"	"	"	0.0768	— 0.25

*Cadmium from Platinum.*—Reference to a paper by Smith and Frankel<sup>1</sup> will disclose the fact that they failed to obtain an electrolytic separation of silver and cadmium from palladium. The separation of silver from platinum succeeds if conducted under the conditions outlined in the preceding example, but the separation of cadmium from platinum resulted negatively, although the current was reduced to 0.2 cc. oxy-hydrogen gas per minute. The precipitated cadmium always contained platinum. We also found that if the platinum dishes were coated with cadmium and the double cyanide of platinum and potassium electrolysed in these vessels, the platinum metal was deposited quite rapidly; cadmium, however, invariably dissolved. This behavior was similar to that observed in the attempted electrolytic separation of cadmium from palladium and from nickel.

Platinum, palladium and nickel show many points of similarity in deportment when their double cyanide solutions are electrolysed.

*Mercury from Platinum.*—This separation is as readily made as that of mercury from palladium and nickel.

	Mercury present. Gram.	KCN. Grams.	Total Dilution.	Current in cc. OH gas per minute.	Platinum present. Gram.	Mercury found. Gram.	Difference in percentage from theory.
32.	0.1902	2.5	150 cc.	0.2 cc.	0.2433	0.1900	— 0.10
33.	"	"	"	"	"	0.1904	+ 0.10
34.	"	"	"	"	"	0.1905	+ 0.15
35.	"	"	"	"	"	0.1910	+ 0.41

<sup>1</sup> This Journal 12, 428.

The separations of gold, silver and mercury from platinum were carried out in the cold. The depositions were made in the same platinum vessels used in the experiments recorded in the first part of this communication. The deposited metals were treated as mentioned in previous papers. The time of precipitation occupied from fourteen to sixteen hours.

CHEMICAL LABORATORY, UNIVERSITY OF PENNSYLVANIA.

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## THE CONSTITUTION OF BENZOQUINONE.—II.

By J. U. NEF.

In a recent paper on this subject,<sup>1</sup> I presented a series of experiments which were so definitely and exclusively in favor of Fittig's formula for quinone, that it seemed as if a doubt concerning the constitution of this substance was no longer admissible. It has been asserted,<sup>2</sup> however, that the proof that quinone dibromide has its bromine atoms in the ortho-position is not positive.

The existence of a para-binding in hydrogenated benzene derivatives has already been rendered very improbable by v. Baeyer's work on benzene,<sup>3</sup> and my own experiments in the anilic acid series<sup>4</sup> have rendered the view based upon the presence of a para-binding in quinone compounds highly improbable. For this reason I pointed out that rhodizonic acid could not possess the constitution first given it by Nietzki, and this conclusion has been confirmed by a recent paper of Nietzki<sup>5</sup> on this subject. There is, therefore, at present not a single fact which points in any way to the existence of a para-binding in benzene or in its hydrogenated derivatives.

That, therefore, quinone dibromide has its bromine atoms in the ortho- and not in the para-position is highly probable, especially since the diagonal ketone-formula was proved untenable by reason of experiments with the anilic acids.

<sup>1</sup> This Journal **12**, 463.

<sup>2</sup> Claus: J. prakt. Chem. [2] **42**, 463; Nietzki: Ber. d. chem. Ges. **23**, 3141; Kehrman: J. prakt. Chem. [2] **43**, 106.

<sup>3</sup> Ann. Chem. (Liebig) **251**, 257, etc.

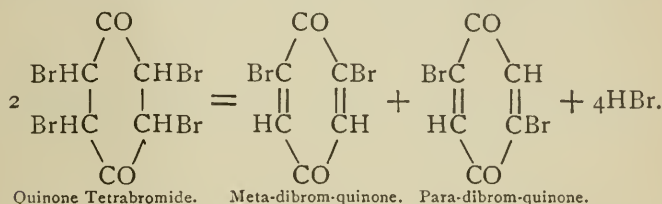
<sup>4</sup> This Journal **12**, 467.

<sup>5</sup> Ber. d. chem. Ges. **23**, 3136.

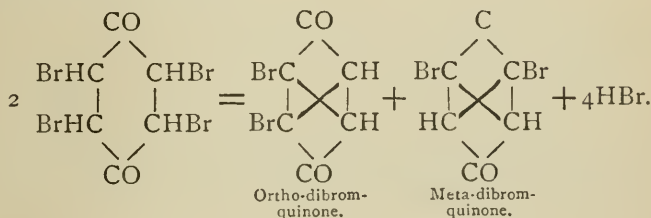


Furthermore, the behavior of quinone di- and tetrabromide towards zinc dust and acetic acid is so analogous to the behavior of v. Baeyer's addition-products of hydrogenated terephthalic acids,<sup>1</sup> especially of 1,2,5 dihydro-terephthalic acid di- and tetrabromide,<sup>2</sup> that there can be little doubt that they are of similar constitution.

The ortho-position of the bromine atoms in quinone dibromide follows also from the behavior of quinone tetrabromide. The latter substance is converted, as I have shown, by boiling with alcohol and water, into meta- and para-dibrom-quinone:



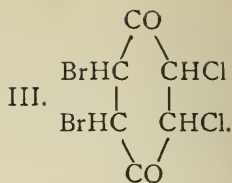
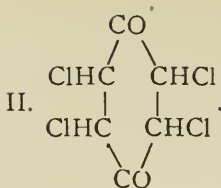
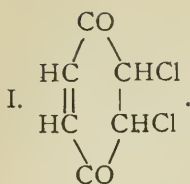
To form these two substances the hydrobromic acid must be split off from ortho-positions: if this splitting-off were to take place from the para-position, only ortho- and meta-dibrom-quinone could be formed:



It follows, therefore, that the hydrobromic acid in quinone tetrabromide is split off from ortho-positions, since not a trace of ortho-dibrom-quinone is formed, but, on the contrary, much para-dibrom-quinone. The conclusion that the addition of bromine takes place in ortho-positions is therefore highly probable. That this is the case I am now able to give further and absolutely conclusive proofs. Mr. T. H. Clark has, under my direction, studied the action of halogens on quinone, and has obtained products whose constitution is to be represented as follows:

<sup>1</sup> Ann. Chem. (Liebig) 245, 103; 251, 257.

<sup>2</sup> Herb. Ibid. 258, 11.



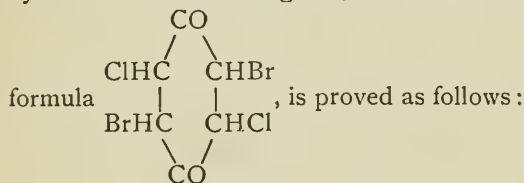
I. Quinone dichloride—pale yellow; melting-point,  $143^{\circ}$ ; distills without change.

II. Quinone tetrachloride—colorless; sublimes without melting and without decomposition.

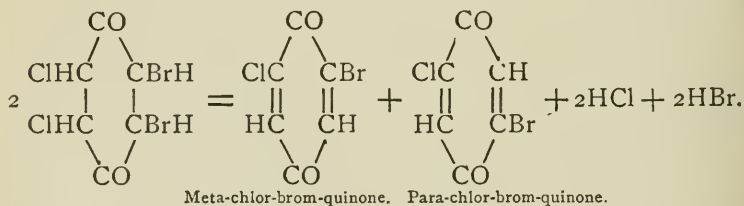
III. Quinone dichloride-dibromide—colorless; melting-point,  $195^{\circ}$ .

These substances are not affected by strong nitric acid, and show the same behavior in all details as the two bromine addition-products already described. The only difference is the greater stability of the chlorine derivatives, which sublime without decomposition.

That the quinone dichloride-dibromide obtained by the action of bromine on quinone dichloride has the constitution represented by the formula above given, and not that represented by the



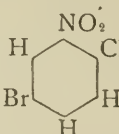
The substance is decomposed by boiling with alcohol and water into about equal parts of meta- and para-chlor-brom-quinone:



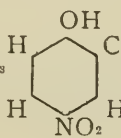
The latter consists of plates which melt at  $172^{\circ}$ ; the former, of needles melting at  $113^{\circ}$ .

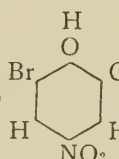
These two isomers were easily separated by fractional crystallisation from ether, wherein the para-compound is the less soluble.

Besides these two isomers no other product was found. That the chlor-brom-quinones obtained have the above-represented constitution was proven by the direct synthesis of these two substances, as follows :

(a). Para-chlor-brom-nitrobenzene,<sup>1</sup> , was reduced

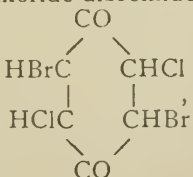
by means of zinc dust and acetic acid to chlor-brom-anilin (melting-point, 43°), and this substance gave, on boiling with manganese dioxide and dilute sulphuric acid, para-chlor-brom-quinone, identical in every particular with the above product, and with a chlor-brom-quinone obtained by Levy and Schultz<sup>2</sup> from chlor-quinone.

(b). Chlor-para-nitro-phenol,<sup>3</sup> , was converted into

brom-chlor-para-nitro-phenol, , (melting-point, 138°),

and this reduced with tin and hydrochloric acid. The tin double-salt of chlor-brom-amido-phenol separates out in flat needles, which, when converted into chlor-brom-amido-phenol sulphate, and boiled with dilute sulphuric acid and manganese dioxide, gave almost quantitatively meta-chlor-brom-quinone, crystallising in needles whose melting-point is 113°, identical in every respect with the corresponding quinone obtained from quinone dichloride-dibromide.

(c). If quinone dichloride-dibromide have its two chlorine atoms

in the para-position, , and it be decomposed by

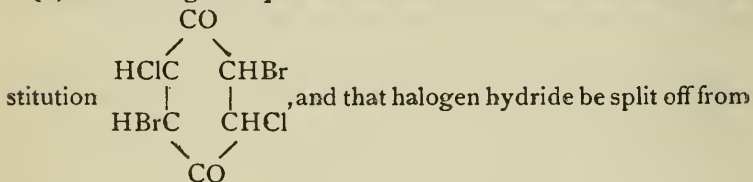
<sup>1</sup> Körner: Jsb. Chem. 1875, 325.

<sup>2</sup> Ann. Chem. (Liebig) 210, 260.

<sup>3</sup> Kollrepp: Ibid. 234, 2.

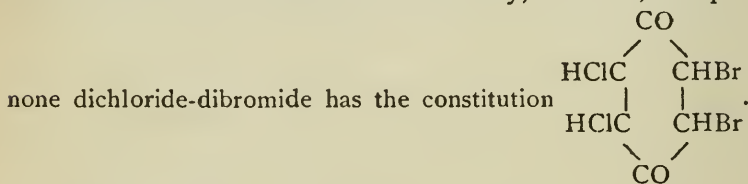
alcohol and water, assuming the splitting off of halogen hydride to take place from ortho-positions, in great part, if not exclusively, the resulting compound would be para-dichlor-quinone (melting-point, 164°), since the chlorine atoms are more firmly bound than the bromine atoms. The other products that might be formed would be para-dibrom-quinone (melting-point, 188°), and meta-chlor-brom-quinone. In the above reaction, however, not a trace of para-dichlor- or of para-dibrom-quinone was found.

(d). Assuming that quinone dichloride-dibromide have the con-



para-positions, only ortho-chlor-brom-quinone and meta-chlor-brom-quinone could be formed.

From the above facts it follows conclusively, therefore, that qui-



The addition of halogens to quinone takes place, moreover, in ortho-positions, and the splitting off of halogen hydride from the addition-products takes place invariably from ortho-positions. These facts can be explained only by Fittig's formula for quinone: their explanation is impossible on the assumption of the diagonal ketone-formula of Claus, and therefore this formula no longer deserves consideration.

The publication of the details of the experimental work of Mr. Clark will take place in this Journal as soon as sufficient material has accrued for a thesis.

I desire to reserve for this laboratory, for the present, the study of the addition-products of quinone.<sup>1</sup> It is already highly proba-

<sup>1</sup> I very much regret the fact that Kehrman's comments (J. prakt. Chem. [2] 43, 106) are full of inaccuracies, as any one can see who will take the trouble to go over the literature of the subject. In my paper (Ber. d. chem. Ges. 20, 2030) I stated definitely that "Die Versuche über die Ersetzbarkeit der Chloratome im Chloranil durch verschiedene andere Radikale werden fortgesetzt." Kehrman's statement, therefore, shows that he has not properly examined into the subject. A number of Kehrman's recent publications have been merely an application of my nitrite-reaction to other chlorinated quinones. (See Ber. d. chem. Ges. 21.





That such a rearrangement of the valences should take place seems to me to be probable for the following reason :

It is impossible to oxidise to the corresponding quinone a number of carboxylated derivatives of hydroquinone, namely, hydroquinone-carboxylic acid or its ether;<sup>1</sup> tolyl-hydroquinone-carboxylic acid or its ether;<sup>2</sup> para-dioxy-terephthalic acid or its ethyl-ester.<sup>3</sup> It seems to me that these facts, which are in themselves very noteworthy, can only be explained when the conversion of hydroquinone into quinone is accompanied not only by a removal of the two hydrogen atoms, but also by a rearrangement of the valences of the carbon atoms forming the closed chain.

CHEMICAL LABORATORY, CLARK UNIVERSITY, April, 1891.

Contributions from the Chemical Laboratory of the Department of Agriculture,  
from H. W. Wiley.

## XIX.—THE BIOLOGICAL FUNCTION OF THE LECITHINES.

(*Preliminary Notice.*)

BY W. MAXWELL.

In an earlier stage of the study of the lecithines I showed, in an article entitled "On the Behavior of the Fatty Bodies, and the Role of the Lecithines during Normal Germination,"<sup>4</sup> that the inorganic phosphorus present in the mature seed, under the action of the processes occurring during incipient growth, becomes reorganised, and appears in the young plantlet in the organic form as a constituent of lecithine.

In the course of continuation of the researches, which have been extended or carried over from the vegetable to the animal organism, I have established the observation that the phosphorus which is present in the organic form as a lecithine in the egg of a hen, under the action of the process of incubation, becomes reorganised, and is found in the form of a mineral phosphate in the bone of the chicken.

<sup>1</sup> Ann. Chem. (Liebig) **237**, 35.

<sup>2</sup> Brünner: Monatsh. Chem. **2**, 464.

<sup>3</sup> Hantzsch and Löwy: Ber. d. chem. Ges. **19**, 26.

<sup>4</sup> This Journal **13**, No. 1.

In the light of the data to be given in a later contribution, of which this is a preliminary notice, it will be possible to indicate the course of the circulation of the element phosphorus in the three divisions of matter, and to show that it is (at least in great part) in the organic form of the lecithine or lecithines that the inorganic phosphorus of the mineral kingdom passes through the vegetable kingdom into the inorganic form, constituting the bone, of the animal kingdom.

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## REVIEWS AND REPORTS.

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GRUNDZÜGE DER THEORETISCHEN CHEMIE. Von Lothar Meyer. Breitkopf und Härtel, Leipzig, 1890. xii + 206 pp. 8vo.

The author of that great work, "Die Modernen Theorien der Chemie," has now given us an introduction to theoretical chemistry. In preparing it he has had in mind not only the needs of students, but of those who are interested in the advance of chemistry in a general way and yet have not the time to follow it in detail. His main effort has been to treat the subject in such a way as to give a general, broad, philosophic conception of it. As might have been expected, the author has admirably accomplished his object. The book is clear and thorough, and can be cordially recommended to those for whom it was written. It differs, of course, in some respects from other similar books that have recently appeared in Germany, while resembling them in other respects. It has most in common with Ostwald's "Grundriss der allgemeinen Chemie," as both emphasize the physical side of chemical phenomena. It is interesting to note that this conservative writer accepts in the main the ideas which have been put forward by Arrhenius, Van't Hoff, Ostwald and others, concerning electrolytic dissociation and osmotic pressure, and that in this introduction he devotes a number of pages to their treatment. It would be hard to find a clearer treatment of these subjects. In regard to the subject of stereo-chemistry, too, the author is in sympathy with the most advanced views. On page 98 he says: "Durch die Einführung der räumlichen, geometrischen Unterschiede in die Structurformeln der organischen Verbindungen haben nicht nur zahlreiche früher unerklärbar scheinende Isomerien eine vollkommen befriedigende Erklärung erfahren; sondern es sind auch noch zahlreiche Beziehungen zwischen der

Atomlagerung und dem Verhalten der Stoffe aufgefunden und aufgeklärt worden, so dass die erst im Jahre 1874 aufgestellte Hypothese vom unsymmetrisch gebundenen Kohlenstoffatome bereits zu den best begründeten Lehren der Chemie gezählt werden darf." The study of such books as this by teachers as well as by students will hasten the arrival of the day when chemistry will be studied as a branch of science.

I. R.

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The Belgian Royal Academy of Science, Literature and Art sends invitations to the leading universities and scientific societies of all countries to join in fitly celebrating the fiftieth anniversary of M. Stas' membership of the Academy. It is proposed to present congratulatory addresses and a gold medal. Jean Servais Stas was born in 1813. He was a pupil of Dumas, and his first publication appeared in the *Annales de Chimie et de Physique* in 1838, on Phloridzin. He has published papers on subjects in organic and inorganic chemistry in the period from 1838 to 1874. He is best known by the one published in 1860 in the *Bulletin* of the Belgian Academy, containing the results of his long and patient studies of the atomic weights of the elements, which have furnished a standard for the subsequent work in this field. The English Royal Society gave him the Davy medal in recognition of the importance of this work.

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FRANCIS CLARK BLAKE died in Helena, Montana, February 21st. Mr. Blake was born in Andover, Mass., in 1854, he graduated at the Worcester Polytechnic Institute in 1876, and in 1877 was appointed Adjunct Professor of Chemistry at Lafayette College. In 1879 he resigned to enter the employ of the Pennsylvania Lead Company, where he remained as assistant superintendent and as superintendent till his death, devoting his energies to the improvement of this extensive refinery.

JAMES BUCKTON MACKINTOSH died in New York, April 15th. Mr. Mackintosh came to this country from England in 1873. His attention was chiefly given to analytical chemistry, especially to the study of the rare earths and of new minerals. He contributed several articles on analytical methods to this journal.

DR. CARL SCHAEGLER died in Berlin, April 24th. Dr. Schaepler was well known as an expert in technological chemistry, and as a writer of books, of which his "*Technologie der Fette und Oele des Pflanzen- und Thierreichs*" and "*Technologie der Fette und Oele der Fossilien*," are known as among the best books on vegetable, animal and mineral oils.





QUANTITATIVE DETERMINATION OF ARSENIC BY THE BERZELIUS-MARSH  
PROCESS STANDARD MIRRORS.



# AMERICAN CHEMICAL JOURNAL.

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## THE QUANTITATIVE DETERMINATION OF ARSENIC, BY THE BERZELIUS-MARSH PROCESS, ESPE- CIALLY AS APPLIED TO THE ANALYSIS OF WALL-PAPERS AND FABRICS.<sup>1</sup>

BY CHARLES R. SANGER.

The original method of Marsh<sup>2</sup> was published in 1836, and in the following year Berzelius<sup>3</sup> proposed the modification which couples his name with that of Marsh. It seems to have escaped notice, at least I can find no mention of the fact, that Berzelius also suggested the quantitative application of the method. He proposed to place some pieces of copper in the reduction-tube, and, after weighing tube and copper, to heat and pass the arsenical gas through. The copper would further the reduction of the arseniuretted hydrogen, and thus the arsenic might be collected and weighed. Wöhler,<sup>4</sup> in 1861, proposes essentially the same method, but heats the tube in two places, at the copper which he uses in the form of a spiral, two inches long, and also just behind the copper, so that whatever gas escapes decomposition by the first heating may be decomposed by the copper. The first practical application of this method seems to have been made by Gautier,<sup>5</sup> in 1876, in the estimation of arsenic contained in tissues.

<sup>1</sup> From the Proceedings of the American Academy of Arts and Sciences. Communicated by the Author.

<sup>2</sup> Edin. Philos. Journ. 21, 229.

<sup>3</sup> Berzelius, Jahresb. 17, 191.

<sup>4</sup> Mineral-analyse, p. 232.

<sup>5</sup> Ann. d'Hygiène publ. et de Méd. légale, 1876, p. 136; also Bull. de la Soc. Chim. [2] 24, 250.

He omits the copper spiral, but heats the reduction-tube by a layer of charcoal 20 to 25 cm. in length. To determine the arsenic deposited, he weighs the tube, dissolves out the mirror by nitric acid, and, after drying, weighs again. Crommydis,<sup>1</sup> a year later, follows Gautier's method in a similar research.

Chittenden and Donaldson,<sup>2</sup> in 1881, investigated this method with very satisfactory results, and suggested the improvements which were necessary for its adoption as a trustworthy analytical method. Their process has found its way into the text-books, and needs no explanation here. I note its use by Hubbard<sup>3</sup> in 1882, and Prescott<sup>4</sup> in 1886, and undoubtedly many others have employed it in toxicological work. It seems remarkable, therefore, that the previous application of the process to quantitative work should have escaped the attention of Kühn and Saeger,<sup>5</sup> as well as Polenske,<sup>6</sup> to whom they refer as the first to propose the method. Kühn and Saeger's article, published a few months ago, contains nothing new; but as the paper of Polenske is inaccessible to me, I cannot say what modification he may have introduced.

I need not refer here to the numerous quantitative methods which depend on the reduction by nascent hydrogen and absorption of the arseniuretted hydrogen by argentic nitrate, the eventual determination of the arsenic being made from the silver solution in a variety of ways. These methods form a class by themselves, and cannot be included in the Berzelius-Marsh process.

All methods for the estimation of arsenic are open to a common objection; they do not allow the estimation of minimal, or even, with accuracy, of small amounts. It happens so often that a small amount of arsenic must remain unestimated, because unweighable, and only an approximation to the real quantity can be made.

In the qualitative analysis of wall-papers and fabrics by the Berzelius-Marsh method, much confusion results from the careless manner of reporting the amount of arsenic which makes its appearance in the reduction-tube. The reports, "trace," "small amount," "large amount," are usually made without reference to any standard mirrors, time of heating the reduction-tube, or, in

<sup>1</sup> Bull. de la Soc. Chim. [2] 25, 348.

<sup>2</sup> This Journal 2, No. 4; Chem. News 43, 21; Moniteur Scient. de Paris, 1881, p. 227.

<sup>3</sup> Physician and Surgeon, Ann Arbor, 4, 348; also Contributions from the Chem. Lab. Univ. Mich., Vol. I, Part I, p. 12.

<sup>4</sup> Chem. News 53, 79.

<sup>5</sup> Ber. d. chem. Ges. 23, 1798.

<sup>6</sup> Arb. a. d. kais. Gesundheitsamt, Bd. V, Heft 2 (1889).

many cases, to the amount of substance taken for analysis. On account of the want of a definite quantitative method which could be easily applied to wall-papers and fabrics, there have been some propositions for a rough quantitative determination, which should serve as a control as to whether the substance contained more or less than a prescribed amount. The Swedish law<sup>1</sup> of 1883, for instance, though not using the Berzelius-Marsh method, prescribes that "440 sq. cm. of the article . . . by reduction with potassic cyanide and sodic carbonate, shall not produce more than a partially opaque mirror in a glass tube of 1.5 to 2 mm. inner diameter." Thoms,<sup>2</sup> in 1883, proposes as a means of control that the results from 100 sq. cm. of paper should be divided into four grades: "strongly arsenical," "arsenical," "traces," and "free." If, when the apparatus has been running ten minutes after the introduction of the solution to be tested, a deposit is obtained no larger than that corresponding to what is produced by 0.1 mgr. of arsenious oxide under similar conditions, the paper may be considered to contain a "trace," and need not be rejected.

A committee of the National Health Association of Great Britain, consisting of Messrs. Bartlett, Heisch, and De Chaumont,<sup>3</sup> suggested, in 1883, that a paper should be considered non-arsenical if, after being treated by a modification of the Berzelius-Marsh method devised by them, it failed to give a mirror in a tube of one-eighth inch internal diameter (about 3.3 mm.) sufficient to cut off at any point a black line of a certain thickness ("thick rule, 8 to pica") on a white ground.

All this is very crude, yet, without a means of easily estimating the amount of arsenic present, it might answer until the exact determination was called for.

The length of time necessary for any of the quantitative methods precludes their use by analysts, especially when, as is generally the case, the quantitative determination is not of especial importance. If we attempt to apply the gravimetric Berzelius-Marsh method to the analysis of wall-paper, we are met, not only by the amount of time necessary for the complete deposition of the arsenic mirror, but by the large amount of paper that must be taken, or,

<sup>1</sup> Correspondence between the English and other Governments respecting the Presence of Arsenic . . . in Wall Papers and Textile Fabrics. Commercial, No. 40 (1883).

<sup>2</sup> Ref. Fres. Zeitschr. 22, 474, from Ber. d. landw. chem. Vers. u. Samencontrolstat. zu Riga, 1883.

<sup>3</sup> Brit. Med. Jour. 1883, p. 1218.

if the proportion of arsenic is very small, the unwieldy amount. Added to this is the necessity for a delicate balance, and also the error in weighing small mirrors of arsenic.

A method is therefore desirable which will allow us to estimate minimal amounts of arsenic, and, in such analyses as that of wall-paper, will give an approximate idea of the amount present without requiring more time than that needed for the proper conduct of the ordinary Berzelius-Marsh method.

The process which is described in the following pages was suggested by Professor H. B. Hill, of Cambridge, about five years ago, and has been in use in that laboratory and others with excellent success. The proof of the availability of the method was undertaken by me, but, owing to numerous interruptions, the completion of the analytical work has been delayed until now.

The method consists, briefly, after getting the arsenic from a measured amount of paper or fabric into solution, in the comparison of the mirror obtained from an aliquot part of the solution with a series of standard mirrors obtained from known amounts of arsenious oxide. No method founded on exactly this principle has ever been fully described, though Otto<sup>1</sup> gives cuts of mirrors obtained from known amounts of arsenious oxide, with which some analysts may have compared their mirrors. Selmi,<sup>2</sup> in 1880, states that he is able to approximate to fractions of a milligram by comparing the mirrors with those obtained from the following amounts: one-twentieth, one-fiftieth, one-hundredth, and one-two-hundredth part of a milligram. Thoms, as stated above, compares his "traces" with a mirror obtained from one-tenth of a milligram, and says that the mirror can be kept any length of time as a comparison standard. Blyth<sup>3</sup> also suggests a comparison of mirrors.

I give in detail the method as I have used it in the analysis of wall-paper, making references to the analytical and experimental work which follows.

*The measurement of the paper* is governed by (a) the quantity of arsenic present, which may sometimes be judged by the color, or by the rough test of the odor from the burning paper, and (b) by the character of the paper; *i. e.* whether a plain color, a small or large figure. I have used 25 sq. cm., 50 sq. cm., and usually 100 sq. cm. As patterns for cutting, thin plates of glass<sup>4</sup> may be

<sup>1</sup> Graham-Otto-Michaelis, Lehrbuch, 2, 2, 520.

<sup>3</sup> Poisons, their Effect and Detection, 1884, p. 534.

<sup>2</sup> Gazz. Chim. Ital. 10, 435.

<sup>4</sup> Dr. Charles Harrington.

used, on which are marked the dimensions. The advantage of the glass is, that the figure of the paper may be seen while the paper is being cut, and also, that, by washing or wiping the glass after each cutting, any danger of contamination by adhering particles from a previous arsenical paper may be avoided. I have used but one plate for 25 sq. cm. ( $5 \times 5$ ); for 50 sq. cm., three ( $5 \times 10$ ,  $4 \times 12.5$ , and  $2 \times 25$ ); and for 100 sq. cm., five ( $10 \times 10$ ,  $5 \times 20$ ,  $4 \times 25$ ,  $8 \times 12.5$ , and  $2 \times 50$ ); such a number allowing the variety in cutting that different papers necessitate.

The paper, cut into small pieces, is placed in a glazed porcelain dish and moistened with 1 to 5 cc., according to the amount of paper taken, of strong sulphuric acid (sp. gr. 1.8) to which has been added about one-thirtieth of its volume of strong nitric acid (Appendix, 2. *e*). The paper and acid are stirred with a thick glass rod until the paper has absorbed the acid, and the dish is then placed on a ring and heated by a low flame, the mixture being stirred continually, until the paper is thoroughly charred (App. 1). This may be determined by the dry "crumbly" appearance, and by the amount of fuming, it being necessary to heat until the nitric acid is expelled. Usually, the first heating is enough, as even if a trace of nitric acid is left, it does no harm (App. 2. *f*); yet, if one has reason to think that considerable nitric acid is held back, it is best, after cooling, to add a few cubic centimeters of water, and heat again until the fumes of sulphuric acid appear. On cooling, the "char" is moistened with a few drops of water, and then about 5 cc. of water are added. The mass is triturated with the thick rod until all lumps are thoroughly broken up, heated to boiling to expel sulphur dioxide (App. 5. *d*) and filtered hot (App. 3).

*Filtration of the Extract.*—In filtering, time is saved and greater accuracy assured by using a filter-pump, and for filtration I have found most convenient a side-neck test-tube of 25 to 30 cc. capacity. This is fitted with a rubber cork through which passes a small funnel, the end reaching just below the side tubulus of the test tube. With the tubulus is connected the pump, and in order to prevent accidental contamination of the tubulus (through which the extract is afterwards poured into the Marsh apparatus), I use a connecting glass tube, which may be rinsed before and after each filtration. This tube is a small U tube not over 25 cm. in total length, with two bulbs blown in the lower part of the U. The



filter-paper is of small diameter, not over 8 cm., and the lot should be tested for arsenic previous to cutting the round filters. As a strengthening cone at the apex will be found convenient for this, as well as for other filtrations, a square piece of cheese-cloth laid under the paper and folded with it.

After filtering, the char is washed with small quantities of hot water until the filtrate and washings fill the test-tube. The extract, after cooling, is ready for weighing or measuring, and introduction into the apparatus.

*The Apparatus.*—Two points will have been noticed in working with the ordinary form of generating flask: the time required for displacement of the air, and the impossibility of governing the evolution of hydrogen during the analysis. The latter objection is partially remedied by some such contrivance as that of Lehmann<sup>1</sup> or of Blondlot,<sup>2</sup> both of whom regulate the current by raising or lowering the zinc by a glass rod working through the cork of the flask. Chittenden and Donaldson<sup>3</sup> regulate the evolution by the successive use of acids of increasing strength. Both difficulties are, however, obviated by the use of a constant hydrogen-generator by which the air of the flask may be swept out and the flow of the hydrogen controlled, thus assuring the uniform rate of deposition of the arsenic, on which the success of the process as a quantitative one largely depends. This idea of a constant generator was apparently first proposed by Verryken,<sup>4</sup> and has been used also in 1888 by Wolff<sup>5</sup> in a modification of Bloxam's electrolytic method.<sup>6</sup> Any form of generator can of course be used. To the delivery-tube is attached a distributing tube, which may be two-way or three-way, according to the number of reduction-flasks used. For two flasks an ordinary Y-tube suffices, each end of the Y being fitted with a thick rubber connecting tube and a screw clamp, so that the supply of hydrogen may be shut off entirely or controlled for each flask. The reduction-flask is a wide-mouthed bottle of about 75 cc. capacity, fitted with a rubber stopper pierced with three holes. Through one hole passes a right-angled tube reaching to the bottom of the flask, the other

<sup>1</sup> Pharm. Zeitschr. f. Russland, 1888, 27, 193.

<sup>2</sup> Mémoires de la Soc. Roy. de Sci., Lett. et Arts de Nancy, 1845.

<sup>3</sup> Loc. cit.

<sup>4</sup> Ref. by Dragendorff, Ermittlung von Giften, 1876, pp. 337 and 317, to Jour. de Pharm. d'Anvers, 1872, pp. 193 and 241.

<sup>5</sup> Ztschr. analyt. Chem. 27, 125.

<sup>6</sup> Ibid.; also Blyth, loc. cit., p. 533.

end being connected with the distribution-tube of the generator. Through the second hole passes the right-angled delivery-tube, reaching just below the rubber cork. The third hole serves for the introduction of acid and extract. Through it passes to the bottom of the flask a tube with the bore at the lower end somewhat reduced by melting.<sup>1</sup> In the top of this tube is set a very small funnel.

To the delivery-tube of the reduction-flask is attached by a rubber stopper a straight bulb drying tube filled with fused calcic chloride (App. 5. *a*), and to the drying tube is connected by a short thick rubber tube the reduction-tube, which should be of the hardest and best quality of Bohemian glass (App. 5. *b*), and of as uniform bore as possible, about 7 mm. inside and 8 mm. outside diameter. It should be drawn out before a small blast-lamp flame to as nearly as possible definite bore, which ought to be from 1.5 mm. to 2 mm. at the place of deposition of the arsenic mirror. The finely drawn tube is bent slightly upward, and sealed at the end.

*The Reagents* (App. 4).—The zinc and sulphuric acid used in the apparatus must be *strictly* free from arsenic, and one should not feel satisfied of their purity unless a stream of hydrogen from the generator, led through the heated tube for several hours, fails to give the slightest deposit. The granulated zinc used in the generator is best of comparatively large size, while that used in the reduction-flasks should be quite fine-grained. The acid should have a concentration of one part strong acid (1.82 sp. gr.) to eight parts of water, though a more dilute acid can often be used.

*The Course of Analysis.*—In the reduction-flask is placed a small quantity, not over three grams, of zinc, and the apparatus is connected together. Tightness must be assured, and can be tested for, if the tip of the reduction-tube is sealed, by adding through the small funnel a few drops of acid. If these do not fall, the tip of the tube is broken off, leaving an opening of not more than 1 mm. diameter, and then about 20 cc. of acid are added. The hydrogen is now turned on from the generator, and, after expulsion of the air, lighted, and the flame turned down to a height of 1 to 2 mm. The evolution of hydrogen should be kept at this rate during the reduction of the arsenical solution. Often it is not necessary to use the generator during the reduction, as the evolution from the reduction-flask is sufficiently rapid. If it

<sup>1</sup> That the fluid introduced may not carry any air with it into the flask.

slackens, the generator may be used again, and indeed it is generally necessary to use it toward the close of the reduction. It may happen, on account of too strong acid or increased action after introduction of the extract, that the evolution is too rapid, and the flask becomes heated (App. 5. *c*). To obviate this, the flask may be set in a vessel fitted with an exit tubulus, and filled with cold water, which can be drawn off and replaced when necessary without disturbing the apparatus. An ordinary crystallising dish with a siphon would answer the purpose.

Shortly after (App. 5. *e*) lighting the hydrogen, the lamp is placed under the heating place and the apparatus tested for absence of arsenic for such length of time as the circumstances direct. In ordinary analyses of wall-paper, I allow 15 to 20 minutes' free run before adding the extract.

The lamp should give a large, clearly defined flame (App. 5. *f*), and should heat the tube with its oxidising flame only. An iron cone may be used for increased draught, but not an iron or glass cylinder, for the greater radius of heat given by the latter tends to throw the mirror farther along the tube, and to deposit it irregularly. A convenient rest for the reduction-tube is made by soldering three stout copper wires to an old binding-screw or post, curving the ends to fit the tube and branching them out, so that the tube lies flat in the curved ends. The binding screw travels vertically on a brass rod melted into a flat, heavy piece of lead, or screwed into the base of an old Bunsen burner.

When the apparatus is found free from arsenic, the extract is added. Previous to this it has been measured or weighed, preferably the latter. The test-tube having its weight marked on it, the weight of the extract is quickly determined. Weighings can be made on a balance sensitive to fifty milligrams, which is enough for all practical purposes.

A few drops of the extract are at first added. If no mirror appears in three or four minutes, one-eighth to one-quarter of the rest may be added, and if in five minutes more there is no mirror, the whole of the extract may be introduced. This cautious addition is necessary in order not to obtain too large a mirror, else a difficulty in estimation might arise, or a new determination might have to be made. A twenty-five minute run is sufficient for the deposition of all the arsenic when the size of the mirror formed in the first fifteen minutes is not larger than that corresponding to 0.05

mgr. of arsenious oxide. If the mirror forming is likely to be larger than this, it is better, after weighing, to start another mirror with another portion of the extract, than to wait for the complete deposition of a mirror which may be too large for comparison with the standards.

*The set of standard mirrors* is made as follows: One gram of arsenious oxide, purified by repeated sublimation, is dissolved with the aid of a little sodic bicarbonate (free from arsenic), and, after acidification with dilute sulphuric acid, is made up to a litre. Of this standard solution (I.), containing 1 mgr.  $\text{As}_2\text{O}_3$  to 1 cc., ten cc. are taken and made up to a litre, giving the standard solution (II.) containing 0.01 mgr. to 1 cc. Of this solution, 1 cc., 2 cc., 3 cc., etc., are carefully measured from a burette and introduced into the reduction-flask of the apparatus, giving the mirrors corresponding to the same number of hundredth-milligrams. It is necessary to make two or more mirrors of the lower amounts, as, even with careful drawing, the cross-sections of the deposition-tubes differ, so that the appearance of the mirror from the same amount of arsenic varies, and the variation is more marked as the mirrors decrease in size. Then, for greater convenience in interpolation, mirrors corresponding to the half-hundredths may be made, so that the set which I use contains the following amounts: 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, and 0.06. Above 0.06 the difference between the mirrors is so hard to estimate with accuracy that it is of no advantage to make any above 0.06. Yet in the set which I have photographed, and which is shown in the plate, the following are added for comparison: 0.07, 0.08, 0.09, 0.10.

When the set is not in use, it should be kept in the dark, and *at no time* be exposed to direct sunlight. Although the tubes be sealed, yet there is sufficient air inside to cause a rapid oxidation in direct sunlight, especially with the lower amounts, and a film of arsenious oxide results. By observing this precaution, the set can be kept a long time without alteration.

The readings of the mirrors are far sharper by transmitted than by reflected light, and comparison should always be made by the former. For this purpose I use, at the suggestion of Professor Hill, a small tin box painted black on the inside and outside, and similar in shape and construction to the old-fashioned stereoscopic camera. The height of the box is 20 cm.; width, 7.5 cm.; length at top, 10 cm.; length at bottom, 15 cm. The bottom is open,

while the top is covered, and fitted with two eyeholes, 2 cm. in diameter and 4 cm. apart. The set of standard mirrors, as shown in the plate, is mounted, by means of sealing wax, in blackened wooden frames, 18 cm. long by about 7 cm. wide, and 4 to 5 mm. thick. The inner dimensions of the frames are 12 cm. by 4.5 cm. The bottom of the box carries a rabbet of tin, on which the frames may be slid, thus bringing the mirrors under the eyeholes. A second rabbet above the first allows the introduction of a frame carrying the mirror to be compared, which may thus be brought between any two of the standards and compared just as in nesslerisation. The box is mounted over a white paper or plate, in front of a good light. The calculation of the amount of arsenic in the area of paper taken follows from the determination of the amount in the aliquot part of the solution. From this can be found the number of milligrams per square meter, which, when multiplied by the factor, 0.0128, gives the number of grains per square yard.

#### APPENDIX.—ANALYTICAL AND EXPERIMENTAL WORK.

The experimental work in the investigation of the availability of the method is given in detail in the following pages.

1. *Necessity of Charring*.—Considerable difference of opinion exists as to the necessity for insuring the absence of organic matter in the extract to be tested. Odling,<sup>1</sup> in 1859, in testing for arsenic in tissues, found that he could obtain arsenic by Reinsch's test in the presence of organic matter, but not by Marsh's. After getting rid of the organic matter by distillation with hydrochloric acid, he had no difficulty with the Marsh test. Blondlot<sup>2</sup> calls attention to the necessity of completely destroying the organic matter. Chittenden and Donaldson,<sup>2</sup> on the other hand, were able, in the presence of organic matter, to detect very small amounts of arsenic, and consider it of no hindrance. My experience has been, that, while the organic matter may not completely prevent the deposition of small amounts, and is no hindrance in the detection of large amounts, yet the character of the mirror is so altered that comparison with the standards is impossible. Besides, the organic matter causes an increased and irregular flow of gas, which tends (App. 5.f) to carry undecomposed arseniuretted hydrogen out of the tube. I therefore take the precaution, by thoroughly charring, to insure the absence of organic matter in the extract.

<sup>1</sup> Guy's Hospital Reports, 5, 367-374.

<sup>2</sup> Loc. cit.



Thoms<sup>1</sup> digests 100 sq. cm. of the paper on the water-bath with (1-7) sulphuric acid, and adds the filtrate directly to the reduction-flask. Fleck<sup>2</sup> considers that digestion with a 25-per cent. sulphuric acid is sufficient to extract the arsenic completely, and Reichardt<sup>3</sup> concurs in this opinion. I cannot agree with this, and consider that the chance of the arsenic being held as arsenious sulphide is alone enough to condemn the method (App. 2. c), not to speak of the organic matter extracted.

2. *Use of an Oxidising Agent in Charring.*—In case the paper contains chlorides, it seemed likely that a portion of the arsenic would be volatilised during the treatment with sulphuric acid. This was found to be true to an extent sufficient to warrant the precaution of adding a small quantity of nitric acid to the sulphuric acid, in order to prevent the formation of arsenious chloride.

a. *The Presence of Chlorides in Wall Papers.*—In order to determine to what extent chlorides exist in wall-papers, several analyses were made of papers taken at random. The method was as follows: A measured amount of paper (400 sq. cm.) was thoroughly moistened with a strong solution of potassic nitrate (free from chlorine) on a broad porcelain plate, dried on the plate, and ignited over the plate. The organic matter was practically destroyed. The residue was transferred from the plate to a chlorine-free filter, and washed thoroughly with hot water. The filtrate, after acidification with dilute sulphuric acid, was boiled to expel nitrous acid, and, after cooling, titrated according to Volhard with approximately hundredth-normal solutions. There is no danger of volatilisation of hydrochloric acid even on prolonged boiling, as Gooch and Mar<sup>4</sup> have shown that a solution containing 0.12 per cent. of hydrochloric acid can be boiled down one-half without appreciable loss. In titrating, as well as in determining the strength of the standard solutions, it was found that the dilution of the solution affected the end-reaction in that the color of the ferric sulpho-cyanate was obscured by that of the argentic chloride, even if the latter were made to "clump together." This difficulty was easily obviated by heating to boiling after adding excess of argentic nitrate, filtering off the chloride, and titrating back in the cooled filtrate. The end-reaction was then as sharp as possible.

Analysis of thirteen papers gave an average of 138 milligrams

<sup>1</sup> Loc. cit.

<sup>2</sup> Rep. analyt. Chem. 1883, Heft 2.

<sup>3</sup> Archiv d. Pharm. 221, 271.

<sup>4</sup> Amer. Jour. Science [3] 39, 293.

of chlorine per square meter, or 1.38 mgr. in the usual amount (100 sq. cm.) taken for the determination of arsenic. The highest amount was 238 mgr., the lowest 56 mgr. In no case was a paper found free from chlorides.

*b. Effect of Chlorides.*—A solution of sodic chloride free from arsenic was made up of such strength that 1 cc. contained 1 mgr. chlorine. Several trials were made of the effect of a known amount of chloride on small amounts of arsenic. 100 sq. cm. S. & S. filter-paper (589) were used in each case. After addition of the arsenic and sodic chloride solutions, the paper was dried in the evaporating dish, and the arsenic determined exactly as described, but without using nitric acid. The following table shows the results obtained. Analyses 1–6 were made with duplicate readings which agreed closely.

	Mgr. $\text{As}_2\text{O}_3$ taken.	Cc. $\text{NaCl}$ , mgr. $\text{Cl}$ , taken.	Mgr. $\text{As}_2\text{O}_3$ recovered.	Percentage $\text{As}_2\text{O}_3$ , recovered.
1	10.0	20.0	5.22	52.2
2	10.0	20.0	4.96	49.6
3	5.0	4.4	3.61	72.2
4	0.5	2.0	0.44	88.0
5	0.1	2.0	0.87	87.0
6	0.05	2.0	0.02	40.0
7	0.01	2.0	0.005	50.0

Analyses 1 and 2 show that the presence of twice the theory of chlorine causes a large loss, with an amount of arsenic comparatively large. Analysis 3 shows a marked loss with less than the theory. Analyses 4 to 7 were made with more chlorine than the average found (1.38 mgr.), but less than the greatest amount (2.38 mgr.); the amounts are respectively 4, 20, 40, and 200 times the theory, and the conditions are more nearly those met with in practice than in analyses 1 to 3. It will readily be seen that the loss is sufficient to warrant the precaution of using an oxidising agent.

*c. Loss by Retention of Arsenic in the Char as Arsenious Sulphide.*—The presence of the sulphide in papers is not very common. Yet papers colored with ultramarine occur frequently, and the sulphuretted hydrogen set free from this by the sulphuric acid acts on the arsenic compound, and thus a large part of the arsenic remains in the char as the sulphide, insoluble in dilute sulphuric acid. The following analyses of a paper are sufficient to show the

danger of loss from this source. The paper had a light blue ground, and the odor of sulphuretted hydrogen was apparent on addition of sulphuric acid. 100 sq. cm. charred with sulphuric acid and a few drops of nitric acid gave an amount of arsenic corresponding to 5.9 mgr. per square meter. 100 sq. cm. charred with sulphuric acid alone gave 4.5 mgr. per square meter. The char was then extracted with ammonia, and the extract evaporated with sulphuric acid and a drop of nitric acid. This yielded 0.01 mgr., corresponding to 1 mgr. per square meter and bringing the total amount up to 5.5 mgr., which agrees with the first analysis.

*d. The Deposition of Arsenic from a Solution of Arsenic Acid.*

—The question arises whether the conversion of the arsenious to arsenic acid by use of an oxidising agent would cause the arsenic to be held back. This was quickly determined by comparison of the standard mirrors with a set prepared from a solution of arsenic acid, of which 1 cc. contained 0.01 mgr.  $\text{As}_2\text{O}_3$ , as  $\text{As}_2\text{O}_5$ . The mirrors agreed sharply. This is at variance with the results of Headden and Sadler,<sup>1</sup> who found, in using the method of Chittenden and Donaldson, that it was necessary to subject the arsenic acid to preliminary reduction in order to obtain all the arsenic present. The reason for this is, probably, that a very small quantity of arsenic acid, such as would occur under the conditions of this method, is more quickly reduced by nascent hydrogen, while the comparatively large quantity used by Headden and Sadler would take more time. They do not show that prolonged treatment in the Marsh reduction-flask would not have eliminated this error.

*e. The Use of Nitric Acid as an Oxidiser.*—Nitric acid suggests itself at once as the most convenient oxidising agent. In this connection may be mentioned the method proposed by Blyth,<sup>2</sup> which consists in soaking the paper in potassic chlorate, drying, burning, and extracting with water. Hager<sup>3</sup> substitutes sodic nitrate for the potassic chlorate. Many destroy the organic matter by hydrochloric acid and potassic chlorate, as in the case of tissues. Lyttkens<sup>4</sup> uses sulphuric acid and potassic chlorate, and Lenz,<sup>5</sup> commenting on this, considers it the best means of treatment of the paper. The German law<sup>6</sup> of 1888 prescribes the treatment of fabrics with strong hydrochloric acid and distillation with ferrous

<sup>1</sup> This Journal 7, 338; Ber. d. chem. Ges. 19, 116.

<sup>2</sup> Loc. cit. p. 532

<sup>3</sup> Pharm. Centralhalle 13, 145.

<sup>4</sup> Ref. Ztschr. analyt. Chem. 22, 147, from Landw. Versuchsstat. 26, 305

<sup>5</sup> Ztschr. analyt. Chem. 22, 147.

<sup>6</sup> Ibid. 27, 471.

chloride. None of these methods in the analysis of wall-papers and fabrics have any advantage over charring with the simple addition of nitric acid, and all require more time.

That all the arsenic may be recovered when nitric acid is used is shown by the following: 0.01 mgr. arsenious oxide was added to 100 sq. cm. of filter-paper and a drop of strong nitric acid added before charring. The mirror obtained corresponded to 0.01 mgr.

1 mgr.  $\text{As}_2\text{O}_3$  and 5 cc. sodic chloride solution (5 mgr. chlorine) were added to 100 sq. cm. filter-paper and treated with a mixture of one part nitric to six parts sulphuric acid. Duplicate readings gave 1.095 mgr. recovered, an error no greater than that which might occur from the method.

10 mgr.  $\text{As}_2\text{O}_3$ , as  $\text{As}_2\text{O}_5$ , were added to 100 sq. cm. filter-paper, and treated with sulphuric acid alone. Duplicate readings gave 9.94 mgr. recovered.

Finally, 100 sq. cm. of a wall-paper containing no arsenic was, after addition of varying amounts of  $\text{As}_2\text{O}_3$ , charred with a nitro-sulphuric acid containing one part nitric to thirty of sulphuric acid. The following table shows the results of four analyses. The readings on 2, 3, and 4 were in duplicate.

	Mgr. $\text{As}_2\text{O}_3$ taken.	Mgr. $\text{As}_2\text{O}_3$ found.	Mgr. per Sq. Meter taken.	Mgr. per Sq. Meter found.
1	0.01	0.009	1.0	0.90
2	0.10	0.0995	10.0	9.95
3	1.00	0.977	100.0	97.70
4	10.00	10.30	1000.0	1030.00

*f. Effect of Free Nitric Acid in the Reduction-flask.*—Rieckher<sup>1</sup> does not consider the presence of free nitric acid to be detrimental, while Fresenius<sup>2</sup> takes the opposite ground. Blondlot<sup>3</sup> thinks that free nitric acid gives rise to the formation of a solid hydride of arsenic on the zinc, thus causing the retention of part of the arsenic. Without discussing the correctness of this statement, which seems to have been quite universally accepted, we have only to consider the effect of a trace of the acid on the deposition of the mirror, as the method of charring would leave, at most, but a very small amount of free nitric acid in the extract. 0.02 mgr. and 0.05 mgr.  $\text{As}_2\text{O}_3$  were added to the reduction-flasks in which were about 20 cc. dilute sulphuric acid, and immediately

<sup>1</sup> Neues Jahrb. f. Pharm. 20, 3.

<sup>2</sup> Ztschr. analyt. Chem. 2, 389.

<sup>3</sup> Comptes Rendus 57, 596.

afterward a drop of strong nitric acid was added to each. The dilution was considerable, but not so great as might occur in practice. The mirrors were clearly defined, and corresponded sharply to 0.02 mgr. and 0.05 mgr. respectively.

3. *Extraction of the "Char."*—It is necessary that the char should be thoroughly pulverised and extracted with *hot* water. Considerable loss is likely to occur if these precautions are disregarded, as the following results show:

To 100 sq. cm. of a wall-paper free from arsenic, 1 mgr.  $\text{As}_2\text{O}_3$  was added, and the char was extracted with 30 cc. cold water. 0.77 mgr. was recovered = 77 per cent.

To the same amount of paper 5 mgr. were added, and the char extracted with 30 cc. cold water. 3.82 mgr. were recovered = 76.4 per cent.

To the same amount of paper 10 mgr. were added, and the char extracted as before, but, in addition, the particles were well triturated. 9.19 mgr. were recovered = 91.9 per cent.

That this loss was not due to error in estimation of the mirrors was shown by repetition of the first two trials, mirrors being obtained from separate portions of the same extract. The char was triturated in each case:—

1 mgr.  $\text{As}_2\text{O}_3$  gave 0.9 mgr. and 0.9 mgr. Average, 90 per cent.

5 mgr.  $\text{As}_2\text{O}_3$  gave 2.92 mgr. and 2.95 mgr. Average, 58.60 per cent.

That arsenic would be left in the char was shown as follows: 100 sq. cm. of paper as above, after addition of 5 mgr.  $\text{As}_2\text{O}_3$ , were charred, and the finely ground mass extracted first with cold water. 3.11 mgr. were recovered = 62.2 per cent. The residue was then extracted with 30 cc. hot water. 1.63 mgr. were recovered = 32.6 per cent. A third extraction with hot water gave a solution free from arsenic. Total amount recovered = 4.74 mgr. = 94.8 per cent.

The quality of the paper has no effect on the loss: 5 mgr.  $\text{As}_2\text{O}_3$  were added to 100 sq. cm. filter-paper and treated as before. Two readings from the same cold extract gave 3.51 and 3.46 mgr. respectively. Average, 69.9 per cent. Finally, to show the practical completeness of extraction with only 25 to 30 cc. hot water, 100 sq. cm. of filter-paper were charred with different amounts of arsenious oxide.



	Mgr. $\text{As}_2\text{O}_3$ taken.	Mgr. $\text{As}_2\text{O}_3$ recovered.			Total.	Percentage $\text{As}_2\text{O}_3$ recovered.
		Extract 1st.	2d.	3d.		
1	5.0	4.99	0.08	0.0	5.07	101.4
2	5.0	4.98	0.07	0.0	5.05	101.0
3	10.1	10.65	0.06	0.0	10.71	106.7
4	10.0	10.37	0.0	...	10.37	103.7

10 mgr. of arsenious oxide per 100 sq. cm. of paper would correspond to 1000 mgr. per sq. meter, which is an unusual amount. Hence any smaller amounts would be easily extracted. It should be borne in mind that the error is necessarily great in such large amounts, for the deposit which is compared with the standards is so small a proportion of the total amount that a slight difference in reading is proportionally increased.

4. *Reagents*.—Many chemists prefer to use hydrochloric acid instead of sulphuric acid, on account of the quicker action of the former on the zinc. Opinions vary considerably as to the error arising from volatilisation of zincic chloride, and consequent deposition at the heating place, when hydrochloric acid is used. Liebig,<sup>1</sup> very soon after the publication of Marsh's method, called attention to possible error from this source, and several years later Wackenroder<sup>2</sup> confirmed Liebig's opinion. Beckurts<sup>3</sup> claims that there is no danger to be feared, but does not show conclusively that this is the case. Brescius<sup>4</sup> recognises the chance of error, and recommends passing the gas through sulphuric acid, if hydrochloric acid is used for generation. The committee of the British Health Association, above referred to, recommends the use of hydrochloric acid, without comment on its possible disadvantage.

While the volatilisation of zincic chloride might not interfere with the detection of arsenic in considerable quantity, yet it is of primary importance in this method for the mirror to be of arsenic alone, and hence capable of comparison with standards. We cannot, therefore, run the risk of the small mirror being contaminated by any impurity whatever. For this reason, if for no other, the use of hydrochloric acid is wholly inadvisable. Then the time gained in using hydrochloric acid is not to be considered in this method, as the use of a constant generator reduces the time of analysis so decidedly.

The same desire to hasten the evolution of hydrogen in the ordinary Marsh process has led to the addition of stimulants to

<sup>1</sup> Ann. Chem. (Liebig) **23**, 217.

<sup>2</sup> Ibid. **222**, 653.

<sup>3</sup> Archiv f. Pharm. **70**, 14.

<sup>4</sup> Dingl. Polyt. Jour. **186**, 226.

the action in the shape of platinic chloride or cupric sulphate. Bernstein<sup>1</sup> has shown that the use of platinic chloride is inadmissible, because arsenic is thereby held back. At the same time, however, he finds no loss when the zinc is platinised or silvered before being used. Headden and Sadler<sup>2</sup> agree with Bernstein in the case of platinic chloride, and find that cupric sulphate also causes a loss. They also get low results by using a spiral of platinum wire in contact with the zinc. Here, again, the use of the constant generator precludes the necessity for increasing the sensitiveness of the zinc.

Mohr,<sup>3</sup> in 1837, called attention to the fact that the residual zinc even after careful washing contained arsenic. This would seem to substantiate the statement of Blondlot, quoted above, concerning the solid hydride of arsenic. Fresenius<sup>2</sup> also considers that the effect of nitric acid is due to the formation of a hydride. When we consider the case of the mere detection of arsenic by the Marsh process, where all the arsenic is not necessarily reduced to arseniuretted hydrogen, it is quite possible that part is left in the zinc, especially if the extract be not free from nitric acid. But in this method, where all of a very small amount of arsenic is to be reduced, and the action is pushed as far as possible, the probability is that no arsenic is left in the zinc. I have often, after deposition of the mirror, pushed the action as far as the complete solution of the zinc, and have never observed any increase of the mirror at the close. It would seem hardly possible for the solid hydride to remain in that state in a reducing medium for such a length of time (compare also 2. *f*). A large amount of carbon in the zinc is apt to cause too rapid evolution, but I cannot confirm the statement of Headden and Sadler<sup>2</sup> that zinc containing carbon causes a loss of arsenic, and that the zinc must in consequence be free from carbon.

5. *General Precautions.*—*a. Means of drying the Hydrogen.*—The use of sulphuric acid is not allowable. I have found the statement of Dragendorff<sup>4</sup> to be true, that sulphuric acid absorbs arseniuretted hydrogen. This is assumed by Janowsky<sup>5</sup> to be due to decomposition into arsenic and hydrogen, but no proof is given. Dragendorff<sup>4</sup> quotes the suggestion of Otto,<sup>6</sup> that a small amount of fused potassic hydroxide be placed before the fused calcic

<sup>1</sup> Inaug. Dissertation, Rostock, 1870.    <sup>2</sup> Loc. cit.    <sup>3</sup> Ann. Chem. (Liebig) **23**, 217.

<sup>4</sup> Ermittlung von Giften, 2te Aufl. p. 336.

<sup>5</sup> Ber. d. chem. Gesell. **6**, 216.

<sup>6</sup> Ausmittlung der Gifte.

chloride, in order to absorb any sulphuric acid which might be carried over, it being possible that the acid might act on the calcic chloride, giving hydrochloric acid, which might form arsenious chloride and thus cause loss of arsenic. The potassic hydroxide would also hold back sulphuretted hydrogen. It is well known that potassic hydroxide absorbs antimoniuiretted hydrogen, and it has been recently shown by Kuhn and Saeger,<sup>1</sup> as well as by Headden and Sadler,<sup>1</sup> that arseniuretted hydrogen is also absorbed by it. There is, however, no need of its use as a precaution against either of the contingencies mentioned above.

Lyttkens<sup>1</sup> considers sulphuric acid to be a better drying agent than calcic chloride, and Lenz<sup>1</sup> agrees with him, but neither shows that there is no loss of arsenic attending its use.

As to Headden and Sadler's<sup>1</sup> statement, unsupported by analysis of the calcic chloride used, that fused calcic chloride holds back arsenic when moist, I have never met with any indication that there was danger of loss from this source.

*b. Impurities in the Glass of the Deposition-tube.*—The errors resulting from the presence of lead and arsenic in glass have been frequently mentioned. The presence of lead in any hard glass fit for use is scarcely probable. The formation of a mirror from either of these sources would, however, be detected at the start, and the glass rejected at once. I have not found any case of error attributable to impurities in the glass.

*c. Temperature of the Reduction-flask.*—Dragendorff<sup>2</sup> quotes Kolbe<sup>3</sup> as having shown that sulphuretted hydrogen is always formed by the action of sulphuric acid on zinc, if the reaction temperature exceeds 30°, and recommends on this account that the flask be cooled. The quotation is misleading. What Kolbe showed—and Fordos and Gélis<sup>4</sup> called attention to the same point some time before Kolbe—was, that if strong acid be added to the flask to increase the action, there was reduction of the acid at the temperature mentioned. With acid diluted with two parts of water no reduction took place. As one would hardly add strong acid to the flask, the danger of formation of sulphuretted hydrogen from mere action of the acid on the zinc is not to be feared. Yet it is necessary to keep the flask cool in some such manner as suggested, if only to prevent too violent action of the acid which may occur from accidental presence of organic matter.

<sup>1</sup> Loc. cit.<sup>2</sup> Loc. cit. p. 336.<sup>3</sup> Ann. Chem. (Liebig) **119**, 174.<sup>4</sup> Comptes Rendus **13**, 437.

*d. Necessity of boiling the Char with Water.*—The formation of a "sulphur mirror" is often met with, due to the decomposition of sulphuretted hydrogen at the heating place. Then, too, Brunn<sup>1</sup> has lately shown that sulphuretted hydrogen and arseniuretted hydrogen form, when heated, hydrogen and arsenious sulphide. The necessity of boiling the char with water is therefore evident, in order that no sulphur dioxide be left in the extract to be reduced by the nascent hydrogen.

*e. Beginning of Heating.*—If the tube be heated as soon as the hydrogen is lighted, the small amount of oxygen left in the flask causes the formation of water in the deposition-tube. This can be avoided, if desired, by waiting a few minutes before setting the lamp under the tube.

*f. Rapidity of Gas-flow and Amount of Heat.*—In the method of Chittenden and Donaldson it is necessary to guard against too rapid evolution of gas, and the heating surface must be very great in order that no arseniuretted hydrogen shall escape decomposition. In this method, the amount of heating surface need not be greater than that given by a good burner, and I have assured myself by direct experiment that no arsenic escapes under the ordinary conditions when the size of the mirror is not above 0.06 mgr. It is necessary, however, for the stream of gas to be slow and regular. Hence the disadvantage of organic matter in the extract, causing an increased and irregular flow of gas.

6. The following table contains some analyses, taken at random, illustrative of the method:—

	Sq. Cm. taken.	Grams Extract.	Gr. Extract taken.	Mirror obtained Mgr. As <sub>2</sub> O <sub>3</sub> .	Mgr. As <sub>2</sub> O <sub>3</sub> found.	Mgr. As <sub>2</sub> O <sub>3</sub> found per Sq. Meter.
1	100	33.17	33.17	0.030	0.030	3.0
2	100	32.27	6.00 5.81	0.017 0.015	0.094 0.083	9.4 8.3
3	100	31.84	5.66 1.90	0.045 0.015	0.253 0.251	25.3 25.1
4	25	29.69	2.64 2.65	0.016 0.017	0.179 0.191	71.9 76.2
5	111.15	33.66	0.78 0.46	0.035 0.020	1.510 1.460	136.0 132.0
6	25	30.67	1.01 2.08	0.040 0.080	1.214 1.180	485.6 472.0
7	12	28.83	0.48 0.61	0.030 0.043	1.802 2.032	1502.0 1693.0

<sup>1</sup> Ber. d. chem. Ges. 22, 3202.

7. *Comparison of Results obtained by the Berzelius-Marsh Process with those obtained by other Methods of Analysis.*—In order to test the availability of the process, it became necessary to analyse, by one of the general quantitative methods, some of the papers which had been analysed by the Berzelius-Marsh method. In the analyses given below, the eventual determination was made by an approximately hundredth-normal solution of iodine, and, when necessary, titrating back with a sodic thiosulphate solution of corresponding strength. I find a similar method to have been proposed some time ago by Holthof.<sup>1</sup> Considerable difficulty was met with at first in finding a suitable method of getting the arsenic from the paper into proper state for titration. A measured piece of paper (100–400 sq. cm.) was treated on a porcelain plate with a strong solution of potassic nitrate, dried on the plate, burned over the plate, and the residue washed off into an evaporating dish. The residue was then treated with about 5 cc. strong sulphuric acid and evaporated until sulphuric acid fumes appeared. To insure the complete expulsion of nitric and nitrous acids, the mass was boiled down again, after addition of a little water. It was then taken up with hot water, filtered, and washed with hot water. The filtrate was kept at 60°–70° for half an hour, and sulphur dioxide passed through. After boiling the reduced solution in the flask until sulphur dioxide was expelled, it was made alkaline with sodic bicarbonate, cooled and titrated. The results obtained were far from satisfactory, but the analyses agreed closely in three cases, which are given below. (Papers numbered 111, 395, and 42 in final table.)

Next, instead of ignition with potassic nitrate, the paper was treated exactly as in the Berzelius-Marsh method, with nitrosulphuric acid (1–30), taking care to get rid of all nitric, and nitrous acids. The extract was reduced at 60°–70° by sulphur dioxide, the excess of the latter driven off by boiling, and the cooled solution made alkaline with sodic bicarbonate, and titrated. In one case the arsenic was precipitated from the extract by sulphuretted hydrogen, and the arsenious sulphide converted to arsenious acid, and titrated. The amount of time required for this, however, offset any advantage from it. Although by care this method can be employed, yet the details require much time and the chances for error are many. Duplicate analyses agreed closely in two

<sup>1</sup> Ztschr. analyt. Chem. 23, 378.



cases, which are given below. (Papers numbered 194 and 155 in final table.)

The method finally used was adapted from the well known process of Schneider<sup>1</sup> and Fyfe.<sup>2</sup> A measured quantity of paper was cut into small pieces and placed in a 500 cc. distilling flask connected with a cooler. Attached to the latter was a receiver with a second tubulus carrying a long tube which served as an air cooler. About 100 cc. of hydrochloric acid, diluted one-half, were added to the flask, and the mixture distilled, slowly, almost to dryness. It was found by trial, that in nearly every case all the arsenic came over in one distillation, and, if not, that a mere trace was left in the residue. The distillate was transferred to a flask, potassic chlorate added, the solution boiled down one-half, transferred to an evaporating dish, and evaporated to dryness, with the addition of a few drops of strong sulphuric acid. The residue was generally white. If dark, from presence of volatile organic matter not destroyed by the potassic chlorate, the addition of a few drops of strong nitric acid and evaporation expelled the organic matter. The residue was then washed into a flask with about 50 cc. water, and reduced and titrated as in the previous cases.

The method was tested by the following analyses of filter-paper to which known amounts of arsenic were added, 200 sq. cm. of paper being used in each case.

	Mgr. As <sub>2</sub> O <sub>3</sub> taken.	Cc. Iodine used. 1 cc. = 0.9815 mgr. As <sub>2</sub> O <sub>3</sub> .	Mgr. As <sub>2</sub> O <sub>3</sub> found.	Percentage As <sub>2</sub> O <sub>3</sub> found.
1 <i>a</i>	5	5.1	5.01	102.1
1 <i>b</i>	5	5.3	5.20	
2 <i>a</i>	5	5.0	4.91	100.1
2 <i>b</i>	5	5.2	5.10	
3 <i>a</i>	25	25.1	24.64	98.4
3 <i>b</i>	25	25.0	24.54	

The residues from the distillations in the last analyses were, after the addition of a few drops of nitric acid, charred with sulphuric acid and "marshed," giving mirrors corresponding to 0.015 mgr. and 0.02 mgr. respectively, showing that a mere trace was left in the flasks.

The following papers were analysed by this method:—

<sup>1</sup> Jsb. Chem. 1851, p. 630.

<sup>2</sup> J. prakt. Chem. 55, 103.

Number of Paper.	Sq. Cm. taken.	Cc. Iodine used. 1 cc. = 0.9815 mgr. $\text{As}_2\text{O}_3$ .	Mgr. $\text{As}_2\text{O}_3$ found per Sq. Meter.
194	200	17.20	844.00
194	200	17.30	849.00
406	400	3.10	76.07
406	400	3.00	73.61
39	400	2.80	68.71
39	400	2.70	66.25
392	380	1.80	46.50
393	400	0.38	9.33
393	400	0.36	8.83
359	400	1.30	31.90
359	400	1.10	27.00

Finally, the following table shows the comparison of the results obtained by the volumetric method with those obtained on the same papers by the Berzelius-Marsh method. The first two columns compare the results in milligrams per square meter, and the second two in grains per square yard. Each result is the mean of two, unless specified.

Number of Paper.	Mgr. $\text{As}_2\text{O}_3$ per Sq. Meter. Berz.-Marsh.	Sq. Meter. Volumetric.	Grains per Sq. Yard. Berz.-Marsh.	' Volumetric.
393	8.8	9.1	0.11	0.12
359	24.0	29.5	0.31	0.38
392	46.8	46.5 <sup>1</sup>	0.60	0.60 <sup>1</sup>
39	64.9	67.5	0.83	0.86
406	72.8	74.9	0.94	0.96
111	110.4	108.7	1.42	1.39
395 <sup>2</sup>	193.0	210.4	2.47	2.69
42	478.8	421.8	6.13	5.40
194	842.0	832.7 <sup>3</sup>	10.78	10.66 <sup>3</sup>
155	1527.1	1478.5	19.55	18.93

Before the above described method was worked out, it was thought that it would give merely an approximation of the amount of arsenic in wall-papers and fabrics, which would allow one, for instance, to pass judgment on the articles from a sanitary standpoint. Not only, as will be seen from the table, does the method give an approximation to the actual amount when ordinarily conducted, but with care it can be made to give results worthy of

<sup>1</sup> One determination.

<sup>2</sup> 395 was a piece of "Turkey red" cloth.

<sup>3</sup> Four determinations.

comparison with other quantitative methods. The greatest error occurs naturally in the estimation of large amounts, but in this case an approximation would answer until a more exact determination was called for.

The process will, I think, be also found of great value in toxicological work, not only as a rapid means of determining the quantity of arsenic present, and as a check on other methods, but also as the only means of accurately determining the amount when the arsenic is present in minute quantity. In such work the organic matter would not generally be charred, but the arsenic would be extracted by the method of distillation. I hope to investigate the extension of the method to toxicological work.

The limit of arsenic that I have been able to detect with certainty by the Berzelius-Marsh method is 0.001 mgr.  $\text{As}_2\text{O}_3$  or 0.0007 mgr. As. I shall not here take up the much discussed question of the delicacy of this as compared with other methods, but I think it will be agreed that no other method enables one to determine quantitatively such small amounts.

In conclusion, I have to thank my assistant, Mr. Charles Walker, very sincerely for his valuable services in most of the analytical work of this paper.

UNITED STATES NAVAL ACADEMY, ANNAPOLIS, MD.,  
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Contributions from the Sheffield Biological Laboratory of Yale University.

## A STUDY OF THE PROTEIDS OF THE CORN OR MAIZE KERNEL.

By R. H. CHITTENDEN, Ph. D., *Professor of Physiological Chemistry in Yale University*, and THOMAS B. OSBORNE, Ph. D., *Chemist at the Connecticut Agricultural Experiment Station.*

The character of the proteids present in the kernel or seed of corn or maize, the most important of American cereals, has up to the present time never been investigated to any great extent. In fact, our knowledge of this subject has been practically limited to the observations of Ritthausen<sup>1</sup> concerning "maize fibrin," a body

<sup>1</sup> Die Eiweisskörper der Getreidearten, Hülsenfrüchte und Ölsamen, Bonn, 1872, p. 113.

soluble in alcohol, and to the bare statement made by Th. Weyl<sup>1</sup> that the powdered seeds of maize yield to a 10-per cent. solution of sodium chloride a globulin-like substance which, after purification by repeated precipitation with water and re-solution in salt water (10 per cent.), coagulates at 75° C. It is a fair presumption, however, judging from the interesting results obtained by Sidney Martin, Vines and other workers among the vegetable proteids, that the proteids of the corn kernel must doubtless be as numerous and complex as those of other seeds already investigated, and this we have indeed found to be the case. In fact, the subject, while more or less fruitful in results, has proved an exceedingly complex one, on account of the large number of different proteids present in the seed, the small quantities present, and the ease with which several of the bodies, especially the globulins, are apparently converted into other forms. Again, in view of the probable widespread distribution of the vegetable proteolytic ferments, any study of the vegetable proteids normally present in seed or fruit must necessarily be complicated by possible ferment changes, through which new bodies may be formed.

Our study of the subject has naturally divided itself into three main parts: 1st, a study of the proteids soluble in salt solutions, but insoluble in water; 2d, a study of the proteids soluble both in water and in dilute salt solutions; 3d, a study of the proteid matter soluble in alcohol, but insoluble in water and salt solutions.

#### I. PROTEIDS SOLUBLE IN SALT SOLUTIONS, BUT INSOLUBLE IN WATER.

Finely ground corn meal<sup>2</sup> extracted with a 10-per cent. solution of sodium chloride yields a slightly opalescent fluid, moderately rich in globulin-like bodies. A simple aqueous extract of ground corn likewise contains more or less globulin held in solution by the salts dissolved from the corn. From both solutions the globulins are slowly precipitated by dialysis of the salts, and partially so by addition of water. They are, moreover, completely precipitated, mixed with other proteids, on saturation of their solutions with ammonium sulphate.

a. *Direct extraction of corn meal with 10-per cent. solution of sodium chloride, and separation of the globulin by dialysis.*

<sup>1</sup> Ztschr. für physiolog. Chem. 1, 84.

<sup>2</sup> All the corn used in these experiments was of one variety, known as White Dent, and was freshly ground to a fine powder prior to each experiment.

In view of the well known action of water, in the presence of possible ferments, on the globulins of some seeds, the first extractions of the corn kernel were made with salt solutions, with a view to diminishing the possibility of cleavage or dissociation of the normal proteids of the kernel. 5 kilos. of finely ground corn meal were therefore soaked in 8 litres of 10-per cent. solution of sodium chloride, with frequent stirring, for 24 hours, after which the fluid was strained off and the residue placed in a screw-press and squeezed dry. A second extraction of the meal was made with 4 litres of fresh salt solution, and the two extracts united. The solution was then filtered through thick filter-paper, yielding an almost perfectly clear yellowish filtrate.

Tested by fractional heat-coagulation a series of coagulums were obtained commencing at about  $35^{\circ}$ – $40^{\circ}$ , a final one making its appearance as the solution was boiled. Further, the clear filtrate from this precipitate gave on addition of acetic acid a flocculent precipitate of proteid matter, all of which may be taken as evidence of the presence of a variety of proteid bodies, coagulable and non-coagulable by heat.

The entire salt solution, with its content of proteids and other substances, was then dialysed<sup>1</sup> in a stream of running water for a period of six days, at the end of which time chlorides were entirely removed. As the percentage of salt in the solution began to diminish a heavy white precipitate made its appearance, which steadily increased in amount as the removal of the salt was continued, leaving a perfectly clear fluid containing some coagulable proteids. The globulin precipitated in this manner was separated from the fluid by decantation, washed somewhat with distilled water, and then redissolved in a 10-per cent. solution of sodium chloride. This latter solution was somewhat turbid even after repeated filtration. A portion tested by heat-coagulation gave the following results: At  $60^{\circ}$  the fluid became decidedly turbid, with formation of flocks at  $64^{\circ}$ . The temperature was then raised to  $68^{\circ}$  and the mixture filtered. The clear filtrate became turbid at  $74^{\circ}$ , with formation of a flocculent precipitate at  $79^{\circ}$ , which was filtered off when the temperature reached  $82^{\circ}$ . The filtrate from this precipitate became turbid at  $83^{\circ}$ , with separation of flocks at  $87^{\circ}$ . The temperature was then raised to  $90^{\circ}$  and the precipi-

<sup>1</sup> During these long periods of dialysis, putrefactive changes were prevented by the occasional addition of a few drops of a 20-per cent. alcoholic solution of thymol.



tate filtered off. This filtrate on being heated to boiling gave no precipitate at first, but as the boiling was continued considerable flocculent matter gradually made its appearance. The largest coagulum was obtained at  $79^{\circ}$ . If we are to trust the results of this fractional heat-coagulation, the natural inference would be that the globulin-like substance separated by dialysis from the sodium-chloride extract of the corn meal is made up of several distinct globulins, or else that the one globulin possibly present is broken apart into several fragments by the action of heat.

The main portion of this sodium-chloride solution of the globulin was dialysed until the salt was entirely removed, a process which took five days and which left the globulin completely precipitated on the sides of the parchment. The peculiar, somewhat granular, appearance of the deposit led us to examine it under the microscope, when it was seen to be composed entirely of spheroids, thus showing a close approach to crystallisation. The precipitate was collected on a filter, washed with water, alcohol and ether, and when air-dried was found to weigh 10.1 grams, thus indicating about 0.2 per cent. of globulin in the air-dry kernel, on the assumption that the extraction and separation were complete. The filtrate from this last separation of the globulin was almost entirely free from proteid matter, giving only a very slight reaction with Millon's reagent, no further separation of any matter by continued dialysis, neither any precipitate on addition of acetic acid or acetic acid and solution of salt, and only the faintest turbidity on boiling.

A portion of the globulin dissolved in 10-per cent. solution of salt yielded by heat-coagulation much the same results as the previous salt solution of the proteid, viz. turbidity at  $58^{\circ}$ , formation of flocks at  $67^{\circ}$ . In the filtrate from this coagulum a second turbidity appeared at  $77^{\circ}$ , followed by flocks at  $87^{\circ}$ . Further, in this filtrate another coagulum appeared on boiling the solution, so that while the individual temperatures of coagulation were somewhat different from the preceding, they point to essentially the same general conclusion.

A portion of the globulin was dried at  $110^{\circ}$  C. until of constant weight, and then analysed with the following results:

*Analysis<sup>1</sup> of Corn Globulin, Preparation A.*

I. 0.3933 gram substance gave 0.2325 gram  $H_2O$  = 6.57 per cent. H, and 0.7250 gram  $CO_2$  = 50.42 per cent. C.

II. 0.3693 gram substance gave 0.2182 gram  $H_2O$  = 6.55 per cent. H, and 0.6845 gram  $CO_2$  = 50.55 per cent. C.

III. 0.3038 gram substance gave 44.1 cc. N at 10° C. and 761.4 mm. pressure = 17.62 per cent. N.

IV. 0.3067 gram substance gave 44.1 cc. N at 8.5° C. and 757.8 mm. pressure = 17.47 per cent. N.

V. 0.5111 gram substance fused with  $KOH + KNO_3$  gave 0.0406 gram  $BaSO_4$  = 1.08 per cent. S.

VI. 0.6773 gram substance fused with  $KOH + KNO_3$  gave 0.0440 gram  $BaSO_4$  = 0.89 per cent. S.

VII. 0.5265 gram substance gave 0.0102 gram ash = 1.93 per cent.

*Percentage Composition of the Ash-free Substance.*

							Average.
C	51.41	51.54	..	..	..	..	51.48
H	6.69	6.67	..	..	..	..	6.68
N	..	..	17.97	17.82	..	..	17.90
S	..	..	..	..	1.10	0.91	1.01
O	..	..	..	..	..	..	22.93
							<hr/> 100.00

b. *Direct extraction of corn meal with 10-per cent. solution of sodium chloride, and separation of the globulin by ammonium sulphate and dialysis.*

25 kilos. of corn meal were extracted with 50 litres of 10-per cent. salt solution, and the residue of meal extracted a second time with 16 litres of salt solution. The two extracts were united, filtered through paper, and the clear fluid saturated with pure ammonium sulphate. This gave rise to a more or less sticky precipitate composed of all the proteids present in the extract. The precipitate so obtained was filtered off, dissolved in water as far as possible, and then treated with 10-per cent. salt solution. The portion remaining insoluble was washed with salt solution as long as anything was removed, and then reserved for further treatment.

The solutions of the ammonium-sulphate precipitate in water (or rather in dilute ammonium sulphate) and in 10-per cent. sodium

<sup>1</sup> Carbon and hydrogen were determined by combustion in a current of oxygen, in an open tube, the vapors passing over a fairly long layer of coarsely granulated oxide of copper, a shorter layer of chromate of lead, and an anterior roll of freshly reduced metallic copper. Nitrogen was determined by combustion with oxide of copper after the Dumas method, while sulphur was estimated by Hammarsten's modification of Liebig's method.

chloride were united and dialysed for two weeks, at the end of which time a large amount of globulin had separated from the solution. The clear fluid, however, still contained some globulin, and was therefore reserved for further examination. The separated globulin was filtered off and redissolved in about 2 litres of 10-per cent. solution of sodium chloride, leaving almost no insoluble residue, and the solution again dialysed until the globulin had separated. This required seven days. The product, after being washed and air-dried, weighed 42 grams, and was composed wholly of spheroids. The filtrate from this latter deposit of globulin was again returned to the dialyser, but failed to give any further separation of globulin even after ten days' continued dialysis.

It is to be observed here that the separation of this globulin from a pure sodium-chloride solution is fairly rapid and quite complete, whereas the presence of ammonium sulphate interferes decidedly with its precipitation by dialysis, doubtless on account of the slower rate of diffusion characteristic of this salt. -

The globulin prepared in this manner was readily soluble in salt solution, leaving only a slight insoluble residue. Subjected to heat-coagulation, the following results were obtained with a moderately large amount of globulin in a 10-per cent. solution of sodium chloride: The solution became turbid at 62°, with separation of flocks at 76.5°. The mixture was then kept at 78° for half an hour, after which it was filtered, the filtrate yielding a further turbidity at 83°, with separation of flocks at 93°. This latter coagulation was considerably heavier than the one at 76°. On boiling the solution, there was a slight increase in the amount of coagulum, which was still further increased by the addition of a drop or two of very dilute acid. Hence, this product shows approximately the same general range of heat-coagulation points as the preceding preparation, separated by simple dialysis from the original sodium-chloride extract. As the salt solution of the globulin showed a faint alkaline reaction, another test was made with a solution of approximately the same strength as the preceding, but carefully neutralised. This solution grew turbid at 64°, with formation of flocks at 76.5°. The mixture was filtered at 77°, and on being heated further became turbid at 82.5°, with separation of flocks at 91°. The filtrate from this latter precipitate became turbid on boiling, and yielded a large precipitate on addi-

tion of acetic acid. It is thus evident that the proteid dissolved in a neutral salt solution cannot be wholly coagulated by heat, even though the heating be continued for some time. In fact, the solution may be evaporated to dryness on a water-bath, the residue taken up again in water, and in the salt solution which results considerable proteid matter will be found dissolved and non-coagulable on further application of heat. In fact, the great bulk of this product appears to be non-coagulable by heat alone. Variations in the proportion of globulin dissolved in the 10-per cent. salt solution modify the temperatures of coagulation only slightly.

A portion of the substance dried at 110° C. until of constant weight was analysed with the following results, which, aside from a slightly higher percentage of carbon, show a close agreement in composition with the corresponding globulin A.

*Analysis of Corn Globulin, Preparation B.*

- I. 0.3500 gram substance gave 0.2180 gram  $H_2O$  = 6.82 per cent. H.
- II. 0.3251 gram substance gave 0.1992 gram  $H_2O$  = 6.81 per cent. H, and 0.6145 gram  $CO_2$  = 51.55 per cent. C.
- III. 0.3717 gram substance gave 0.7021 gram  $CO_2$  = 51.52 per cent. C.
- IV. 0.3592 gram substance gave 50.5 cc. N at 2.5° C. and 769.1 mm. pressure = 17.73 per cent. N.
- V. 0.7523 gram substance fused with KOH +  $KNO_3$  gave 0.0472 gram  $BaSO_4$  = 0.86 per cent. S.
- VI. 0.7871 gram substance fused with KOH +  $KNO_3$  gave 0.0491 gram  $BaSO_4$  = 0.85 per cent. S.
- VII. 0.4622 gram substance gave 0.0025 gram ash = 0.54 per cent.

*Percentage Composition of Ash-free Substance.*

							Average.
C	..	51.83	51.80	..	..	..	51.82
H	6.85	6.84	..	..	..	..	6.85
N	..	..	..	17.82	..	..	17.82
S	..	..	..	..	0.86	0.85	0.86
O	..	..	..	..	..	..	22.65
							<hr/>
							100.00

Another sample of globulin was prepared as follows: 2.5 kilos. of ground corn were extracted with about 10 litres of 10-per cent. solution of sodium chloride, and the extract, together with the washings, after filtration, saturated with ammonium sulphate. The precipitate was dissolved as far as possible in water and in 10-

per cent. salt solution, and the united filtrates dialysed until free from chlorides. The deposit of globulin, which gradually formed, was filtered off, washed with alcohol and ether, and dried at  $110^{\circ}$  C. until of constant weight.

On analysis it gave the following results :

*Analysis of Corn Globulin, Preparation C.*

I. 0.2307 gram substance gave 0.1442 gram  $H_2O$  = 6.95 per cent. H, and 0.4330 gram  $CO_2$  = 51.17 per cent. C.

II. 0.3528 gram substance gave 51.5 cc. N at  $11.5^{\circ}$  C. and 745.6 mm. pressure = 17.26 per cent. N.

III. 0.3000 gram substance gave 0.0028 gram ash = 0.93 per cent.

*Percentage Composition of the Ash-free Substance.*

			Average.
C	51.64	..	51.64
H	7.01	..	7.01
N	..	17.42	17.42
S } O }	..	..	23.93
			<hr/> 100.00

Still another preparation of globulin was separated in the following manner: 2.5 kilos. of corn meal were extracted with 12 litres of 5-per cent. solution of ammonium chloride, the residue of meal re-extracted with more ammonium-chloride solution, and the united filtrates precipitated with ammonium sulphate. This precipitate was dissolved as far as possible in water and 5-per cent. ammonium-chloride solution, leaving only a small insoluble residue, and the united fluids dialysed in running water for seven days. The globulin which separated was then dissolved in 10-per cent. solution of sodium chloride and redialysed until the salt was entirely removed. The precipitated globulin was then washed with water, alcohol and ether, and after being dried at  $110^{\circ}$  C. was analysed with the following results :

*Analysis of Corn Globulin, Preparation D.*

I. 0.1289 gram substance gave 0.0781 gram  $H_2O$  = 6.74 per cent. H, and 0.2432 gram  $CO_2$  = 51.43 per cent. C.

II. 0.2639 gram substance gave 39.1 cc. N at  $11^{\circ}$  C. and 746.5 mm. pressure = 17.57 per cent. N.

III. 0.2561 gram substance gave 0.0012 gram ash = 0.47 per cent.



*Percentage Composition of the Ash-free Substance.*

			Average.
C	51.67	..	51.67
H	6.77	..	6.77
N	..	17.65	17.65
S	..	..	} 23.91
O	..	..	
			<hr/> 100.00

In these four preparations we have a good illustration of the general character of the globulin obtainable from the corn or maize kernel by direct extraction with salt solution. The product appears to be the same whether directly separated from its saline solution by dialysis, or first precipitated by ammonium sulphate and then separated by dialysis. The chemical composition of the four preparations is essentially identical, as seen from the accompanying table:

	Globulin A.	Globulin B.	Globulin C.	Globulin D.	Average.
C	51.48	51.82	51.64	51.67	51.65
H	6.68	6.85	7.01	6.77	6.82
N	17.90	17.82	17.42	17.65	17.69
S	1.01	0.86 }	23.93	23.91	0.93
O	22.93	22.65 }			22.91
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Many things, however, point to the view that the corn globulin separated from the kernel by the above methods is not a single substance, although we must continually keep in mind the possibility of unknown methods of cleavage which may perchance be facilitated by the very processes made use of in testing the globulin. Foremost among these is the peculiar and more or less variable range of coagulation-points obtained whenever a sodium-chloride solution of the globulin is subjected to fractional heat-coagulation. From the data thus obtained we might argue a variable mixture of phyto-myosin, vitellin, and some non-coagulable globulin. As to myosin, however, saturation of a salt solution of the globulin with salt crystals gives only a small precipitate, indicating but little of this substance. The next point suggestive of mixture is the fact that a portion of the globulin readily undergoes change into an insoluble modification by contact with water or strong salt solutions, while another portion is apparently very resistant to such action. Thus, in the precipitation of the globulin

by saturation with ammonium sulphate or by dialysis, more or less insoluble matter is formed (insoluble in 10-per cent. salt solution), but this amount grows less and less as the process is repeated, being apparently co-extensive with the amount of this changeable globulin present. The bulk of the globulin, however, retains its solubility in salt solutions by this treatment, under ordinary circumstances.

*c. Fractional separation of the above corn globulin by various methods.*

Treatment of the purified globulin with 10-per cent. salt solution, as stated above, almost invariably shows the presence of at least a small amount of substance insoluble in salt solution, possibly due to a partial conversion of the globulin into an albuminate by the action of water. It was further found that addition of water to a 10-per cent. salt solution of the globulin was followed by only a partial precipitation of the proteid. Hence an attempt was made to separate the globulin into three fractions for analysis. Accordingly, 5-6 grams of the air-dry globulin, Preparation A, were treated with about 300 cc. of a 10-per cent. solution of sodium chloride, and the insoluble matter collected on a filter and washed thoroughly with 10-per cent. salt solution. This residue was finally washed with water until the salt was entirely removed, then with alcohol and ether. It weighed 0.57 gram (Preparation A<sup>1</sup>).

The salt solution and washings containing the bulk of the globulin, amounting to 430 cc., were diluted with distilled water to 4300 cc., by which an abundant precipitate was obtained. This was allowed to settle, then collected on a filter, washed free from chlorides, and lastly with alcohol and ether. It weighed 1.87 grams (Preparation A<sup>2</sup>).

The dilute salt solution containing the remainder of the globulin, representing the more soluble portion, was dialysed in running water until the salt was entirely removed, at the end of which time the globulin had separated wholly in the form of *spheroids*. It was collected on a filter, washed with water, alcohol and ether, and weighed 1.6 grams (Preparation A<sup>3</sup>).

These three fractions were dried at 110° C. until of constant weight, and analysed with the following results:

*Analysis of Preparation A<sup>2</sup>.*

I. 0.5068 gram substance gave 0.3082 gram H<sub>2</sub>O = 6.75 per cent. H, and 0.9540 gram CO<sub>2</sub> = 51.34 per cent. C.

II. 0.3622 gram substance gave 53.5 cc. N at 8° C. and 759.6 mm. pressure = 18.01 per cent. N.

III. 0.2994 gram substance gave 0.0025 gram ash = 0.83 per cent.

*Percentage Composition of the Ash-free Substance.*

			Average.
C	51.76	..	51.76
H	6.80	..	6.80
N	..	18.16	18.16
S	..	..	} 23.28
O	..	..	
			<hr/>
			100.00

*Analysis of Preparation A<sup>3</sup>.*

I. 0.2220 gram substance gave 0.1382 gram H<sub>2</sub>O = 6.91 per cent. H, and 0.4132 gram CO<sub>2</sub> = 50.76 per cent. C.

II. 0.3221 gram substance gave 47.5 cc. N at 6° C. and 762.6 mm. pressure = 18.19 per cent. N.

III. 0.3318 gram substance gave 49.3 cc. N at 5.8° C. and 754.2 mm. pressure = 18.14 per cent. N.

IV. 0.2977 gram substance gave 0.0022 gram ash = 0.74 per cent.

*Percentage Composition of the Ash-free Substance.*

				Average.
C	51.13	..	..	51.13
H	6.96	..	..	6.96
N	..	18.32	18.27	18.30
S	..	..	..	} 23.61
O	..	..	..	
				<hr/>
				100.00

*Analysis of Preparation A<sup>1</sup>.*

I. 0.3030 gram substance gave 36.5 cc. N at 5.8° C. and 758.8 mm. pressure = 14.79 per cent. N.

II. 0.1914 gram substance gave 0.0112 gram ash = 5.85 per cent.

Percentage of nitrogen in the ash-free substance = 15.59.

The following table shows the relationship of the several products:

	The original globulin. A.	Portion soluble in the dilute NaCl. A <sup>3</sup> .	Portion insoluble in the dilute NaCl. A <sup>2</sup> .	Portion insol. in 10-per ct. NaCl. A <sup>1</sup> .
C	51.48	51.13	51.76	..
H	6.68	6.96	6.80	..
N	17.90	18.30	18.16	15.59
S }	1.01	23.61	23.28	..
O }	22.93			
Ash	1.93	0.74	0.83	5.85

From this it is to be seen that while there is no very radical point of difference in composition between the first three products, there are changes in the relative percentages which are strongly suggestive of admixture. Certainly that portion of the original globulin insoluble in 10-per cent. salt solution has a noticeably low percentage of nitrogen, surely low enough to account for the slightly higher percentages of nitrogen in the products A<sup>3</sup> and A<sup>2</sup>. From the data here offered there is no positive evidence as to whether A<sup>1</sup> is an alteration-product of the original globulin, or whether it simply represents a small impurity. The former view is certainly the more plausible one, however, especially when it is remembered that this globulin had been dissolved in a salt solution and filtered two or three times previously. Again, it is to be noticed in comparing the two soluble products A<sup>2</sup> and A<sup>3</sup>, that the body containing the lower percentage of nitrogen contains the higher percentage of carbon; and further, that in both products the percentage of nitrogen is by this treatment raised so as to correspond closely with the nitrogen content of pure phytovitellin.

In view of these results a portion of corn globulin was next separated into a number of fractions by the solvent action of various strengths of salt solution, and the several fractions studied, especially with reference to their composition and heat-coagulation points.

The globulin (Preparation E) was made from 5 kilos. of freshly ground corn by direct extraction with an abundance of 10-per cent. solution of sodium chloride, the proteids precipitated by saturation of the filtered solution with ammonium sulphate, this precipitate dissolved in water and salt solution, and the filtered fluid dialysed in running water for one week until the globulin had separated.

The entire quantity of globulin, about 10 grams, was then treated directly with one litre of 0.25-per cent. solution of sodium chloride at the temperature of the room and kept in agitation for about 3 hours. The residue was then filtered off and extracted again with one litre of salt solution of the same strength, the solution being kept in contact with the globulin for about 18 hours. This was likewise filtered off and the residue again extracted with two litres of 0.25-per cent. salt solution. A portion of the combined extract obtained in this manner, on being heated, grew

slightly turbid at 54°; this turbidity was still slight at 63°, but at 71° a flocculent coagulum appeared. No further coagulum appeared until the solution was boiled, and then only a slight one. The filtrate from this precipitate gave a faint reaction with acetic acid and potassium ferrocyanide. These united extracts were then placed in dialysers and dialysed in running water until the salt was entirely removed, when the deposited globulin was filtered off, and washed with alcohol and ether. It weighed air-dry 0.18 gram (Preparation E<sup>1</sup>).

That portion of the globulin insoluble in 0.25-per cent. salt solution was placed in two litres of 0.5-per cent. solution of sodium chloride, and kept in contact with it for 18 hours or longer at 20° C., after which it was filtered off and treated with a fresh portion of salt solution of the same strength. The extract so obtained became turbid at 56°, and gave a flocculent coagulum at 75°. The filtrate from this coagulum became slightly turbid on boiling and gave a slight precipitate with acetic acid and potassium ferrocyanide. On dialysis of the 0.5-per cent. salt solution 0.527 gram of air-dry globulin was obtained (Preparation E<sup>2</sup>).

The remainder of the globulin was next treated with 0.75-per cent. salt solution at 20° C. until all soluble matter was removed. A portion of the solution so obtained, on being heated, became turbid at 59°, with separation of flocks at 72.5°. The filtrate from this coagulum became turbid again at 79° and flocked at 85°. On boiling this filtrate a little more precipitate appeared. By dialysis of the united filtrates 2.32 grams of globulin were obtained (Preparation E<sup>3</sup>).

The globulin still undissolved was then treated, after the manner described, with 1.0-per cent. salt solution as long as anything dissolved. This extract coagulated as follows: it became faintly turbid at 63°, with separation of flocks at 79.5°. The filtrate gave a second turbidity at 85°–87°, which increased slightly on boiling. By dialysis, 2.9 grams of globulin were obtained (Preparation E<sup>4</sup>).

The residue of the original globulin was next treated with two litres of 2.0-per cent. salt solution, in which it nearly all dissolved. The slight residue was rejected. The extract coagulated as follows: turbid at 79°, with formation of flocks at 90°. The filtrate grew turbid again at 94°, with separation of flocks at 99°. On dialysis of the solution 2.2 grams of globulin were deposited (Preparation E<sup>5</sup>). This substance, on being tested anew with 1.0-per cent. salt solution, was found practically insoluble.



The several products enumerated were dried at 110° C. until of constant weight, and then analysed with the following results :

*Analysis of that Portion of the Globulin Soluble in 0.25-per cent. Solution of Sodium Chloride (E<sup>1</sup>).*

I. 0.1594 gram substance gave 21.6 cc. N at 4.0° C. and 772.3 mm. pressure = 17.04 per cent. N.

Not enough substance for an ash determination.

*Analysis of that Portion of the Globulin Soluble in 0.5-per cent. Solution of Sodium Chloride (E<sup>2</sup>).*

I. 0.2470 gram substance gave 34.9 cc. N at 3.0° C. and 763.3 mm. pressure = 17.63 per cent. N.

II. 0.2170 gram substance gave 0.0075 gram ash = 0.69 per cent. ash.

Percentage of nitrogen in the ash-free substance = 17.74.

*Analysis of that Portion of the Globulin Soluble in 0.75-per cent. Solution of Sodium Chloride (E<sup>3</sup>).*

I. 0.3303 gram substance gave 0.2018 gram H<sub>2</sub>O = 6.79 per cent. H, and 0.6300 gram CO<sub>2</sub> = 52.02 per cent. C.

II. 0.3222 gram substance gave 0.1987 gram H<sub>2</sub>O = 6.86 per cent. H, and 0.6125 gram CO<sub>2</sub> = 51.84 per cent. C.

III. 0.4261 gram substance gave 61.5 cc. N at 4.2° C. and 750.2 mm. pressure = 17.62 per cent. N.

IV. 0.3042 gram substance gave 42.9 cc. N at 3.0° C. and 764.1 mm. pressure = 17.61 per cent. N.

V. 0.4353 gram substance gave 0.0023 gram ash = 0.53 per cent.

*Percentage Composition of the Ash-free Substance.*

					Average.
C	52.25	52.07	..	..	52.16
H	6.82	6.89	..	..	6.86
N	..	..	17.69	17.68	17.69
S	..	..	..	..	} 23.29
O	..	..	..	..	
					100.00

*Analysis of that Portion of the Globulin Soluble in 1.0-per cent. Solution of Sodium Chloride (E<sup>4</sup>).*

I. 0.3057 gram substance gave 0.1900 gram H<sub>2</sub>O = 6.90 per cent. H, and 0.5814 gram CO<sub>2</sub> = 51.87 per cent. C.

II. 0.5543 gram substance gave 76.0 cc. N at 3.3° C. and 774.2 mm. pressure = 17.33 per cent. N.

III. 0.3593 gram substance gave 50.0 cc. N at 3.0° C. and 754.3 mm. pressure = 17.16 per cent. N.

IV. 0.4353 gram substance gave 0.0023 gram ash = 0.53 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	52.14	..	..	52.14
H	6.93	..	..	6.93
N	..	17.43	17.26	17.35
S	..	..	..	} 23.58
O	..	..	..	
				<hr/> 100.00

*Analysis of that Portion of the Globulin Soluble in 2.0-per cent. Solution of Sodium Chloride (E<sup>6</sup>).*

I. 0.3705 gram substance gave 0.2263 gram H<sub>2</sub>O = 6.79 per cent. H, and 0.6995 gram CO<sub>2</sub> = 51.50 per cent. C.

II. 0.3632 gram substance gave 0.2209 gram H<sub>2</sub>O = 6.76 per cent. H, and 0.6850 gram CO<sub>2</sub> = 51.46 per cent. C.

III. 0.4940 gram substance gave 70.3 cc. N at 3.0° C. and 755.4 mm. pressure = 17.57 per cent. N.

IV. 0.3434 gram substance gave 0.0028 gram ash = 0.81 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.92	51.88	..	51.90
H	6.84	6.81	..	6.83
N	..	..	17.71	17.71
S	..	..	..	} 23.56
O	..	..	..	
				<hr/> 100.00

The first thing to be noticed from these results is that only a comparatively small amount of the original globulin is soluble in very weak salt solutions. It is not until the solution contains 0.75 per cent. of salt that much globulin is dissolved. It is further noticeable that the weaker salt solutions have throughout a lower coagulation-point than the stronger salt solutions, and, moreover, that no one of the extracts coagulates completely at a given temperature, but shows some evidence, by a turbidity at least, of several different heat-coagulation points. As regards composition, the nitrogen of the several fractions is practically the same, and as this is apt to be the most variable element in proteid bodies, it is probable that the several fractions have essentially the same composition. It is further noticeable that the composition of the fractions E<sup>3</sup>, E<sup>4</sup> and E<sup>5</sup> is practically identical with the composition of the globulins A and B, although the average content of carbon

in the former products is a trifle higher. Of the 10 grams of air-dry globulin started with, in this experiment, 8.12 grams were recovered in the several fractions. There was obviously some loss, especially in the many filtrations, so that this deficiency is not to be considered as representing the amount of globulin or alteration product insoluble in the 2.0-per cent. salt solution. The actual amount of insoluble matter was certainly far smaller than this.

It would have been interesting to have determined the percentage of nitrogen in the insoluble portion, but the quantity was so small and it was so mixed with shreds of filter-paper that the result in this case could have had little value.

The relationship of these several fractions or portions of the original globulin is clearly shown in the following table:

Portion soluble in NaCl	0.25 per ct.	0.50 per ct.	0.75 per ct.	1.0 per ct.	2.0 per ct.
C	..	..	52.16	52.14	51.90
H	..	..	6.86	6.93	6.83
N	17.04	17.74	17.69	17.35	17.71
S } O }	..	..	23.29	23.58	23.56
Coagulation-points, <sup>1</sup> 1st.	54°, 71°	56°, 75°	59°, 72.5°	63°, 79.5°	79°, 90°
" " 2d.	..	..	79°, 85°	85°, 87°	94°, 99°

This experiment, then, so far as it goes, corroborates the idea that the original globulin is a mixture of closely allied bodies possessed of different heat-coagulation points and of different degrees of solubility in dilute salt solutions. This method of treatment, however, is insufficient to bring about a complete separation of the individual bodies, the separate fractions obtained above being evidently themselves more or less mixtures, as indicated by their heat-coagulation points and their resemblance in chemical composition. This might indeed be possible, even if there were only two globulins present, for, as is well known, it is often as difficult to bring about a sharp separation of certain proteid bodies, having many points in common, as it is to separate a mixture of several fats.

[To be continued.]

<sup>1</sup> The first figure of each pair represents the appearance of a turbidity, the second figure the formation of flocks.

Contributions from the Chemical Laboratory of the Department of Agriculture,  
from H. W. Wiley.

## XX.—ON THE NITROGENOUS BASES PRESENT IN THE COTTON SEED.

BY W. MAXWELL.

The nitrogenous bases choline and betaine have been shown to be present in the cattle foods prepared from the cotton seed. Choline was discovered in a sample of those foods by Prof. R. Böhm, in the year 1881.<sup>1</sup> Böhm states having received from a druggist an alcoholic extraction of a cattle food prepared from cotton seed, which food, on being fed as a diet to young cattle belonging to a farmer in Germany, had proved fatally poisonous. From the "alcoholic extraction" a large preparation of choline was obtained; but Prof. Böhm concluded that no other alkaloidal principles were present.

In the year 1882 a preparation of betaine was separated from the foods made from cotton seed by Prof. Ritthausen and Dr. Weger.<sup>2</sup> The discovery of the latter nitrogenous base, and admixed with unknown proportions of choline, has made it appear desirable that a revision of the investigations made by the given authorities should be undertaken, and particularly on account of the different toxical properties ascribed to choline and betaine.

Prof. Gaehtgens, during experiments conducted in order to establish the toxical or non-toxical property of choline,<sup>2</sup> observed that when 0.3 gram of choline was given to a strong cat, an immediate paralysis occurred. Further, when 0.5 gram was administered to an equally vigorous cat, death was almost instantaneous. So far it has been believed that betaine is a non-poisonous base; but the experiments made with betaine, in respect of its toxical properties, could be revised with some advantage.

It has thus appeared important to determine whether choline or betaine is present in the cotton seed, and the foods prepared from the seed in greatest quantity, and to estimate, approximately at least, the quantity of each of those bodies contained. And not only from a scientific standpoint is it desirable, but even more strongly so from a practical view, as the foods prepared from the

<sup>1</sup>Address before the Scientific Society in Marburg.

<sup>2</sup>J. prakt. Chem. 30.

<sup>2</sup>Dorpat. med. Zeitschrift, Bd. I, 1870.

cotton seed are used very extensively as a common article of diet for cattle.

The investigations were conducted as follows: About five pounds of finely ground cotton-seed cakes were extracted with 70-per cent. alcohol. The reason for extracting the material with dilute alcohol instead of using very dilute solutions of mineral acid was to avoid any possible action of the acid upon the choline, by which means the latter could be in part converted into betaine. After separation from the material, the extract was distilled and the residue taken up in water. The aqueous solution was treated with lead acetate, the lead precipitate separated by filtration, and the excess of lead removed from the filtrate and the latter evaporated down to a sirupy residue. This residue was then extracted with 70-per cent. alcohol containing 1-per cent. hydrochloric acid, in which menstruum the alkaloidal bodies were taken up. The alcohol-hydrochloric acid extraction was brought into a deep beaker, and an alcoholic solution of mercuric chloride added. Instantly on adding the mercuric chloride an almost pure, white double salt of the nitrogenous bases began to separate out.

After standing for 10 days a large preparation of the mercury-chloride double salts was separated from the liquid, the latter being set aside, and after standing some weeks a second crop of crystals was obtained. The double salts were dissolved in, and recrystallised out of, water, and after decomposition by means of hydrogen sulphide the sulphide of mercury was removed by filtration. The filtrate containing the hydrochlorates of the bases was very slowly evaporated to a small volume, and then placed in a desiccator over sulphuric acid until the crystallisation of the salts was complete. The hydrochlorate salts were free from color and in the form of lucid and well-developed crystals. After all moisture had been absorbed from the crystals they were saturated with an ample volume of absolute alcohol. In absolute alcohol the hydrochlorate of choline went into solution with some small portion of the betaine salt. By this method an approximate estimation of the relative proportions of choline and betaine was obtained.

In order to obtain a quantitative estimation of the relative proportions of choline and betaine 7.248 grams of the hydrochlorate salts (water-free) were taken and treated with absolute alcohol. As it has been remarked, all the choline hydrochlorate salt was dissolved and some portion of the betaine salt. The alcohol solu-



tion of the choline salt was evaporated to dryness and re-extracted with absolute alcohol three times, when it was found that the hydrochlorate of choline was obtained practically free from betaine. The results obtained by this method of separation were as follows:

Choline hydrochlorate = 1.08 grams.

Betaïne                   "                   = 6.168 grams.

In the sample of cattle food, prepared from the cotton seed upon which this work has been done, the bodies choline and betaine appear to be present in the following relative proportions:

Choline = 17.5 per cent.

Betaïne = 82.5       "

The alcohol solution of the hydrochlorate of choline was treated with platinum chloride, and, after recrystallisation of the precipitate, a fine preparation of the platinum double salt of choline was obtained. A portion of the platinum double salt was broken up by means of hydrogen sulphide, and, after separation of the sulphide by filtration, the water solution of the hydrochlorate of choline gave the following characteristic reactions:

With 1. Phospho-tungstic acid, white precipitate.

2. Phospho-molybdic acid, yellow precipitate.

3. Bismuth-potassium iodide, red precipitate.

4. Cadmium-potassium iodide, grey precipitate and was recrystallised.

5. Iodine, brown precipitate and was recrystallised.

6. Platinum chloride, yellow precipitate soluble in water.

The hydrochlorate of betaine, after separation of the choline salt as already stated, was further treated in order to obtain a preparation of pure betaine. The aqueous solution of the betaine salt was treated with phospho-tungstic acid, when a phospho-tungstate of the base was obtained. The latter salt was broken up with calcium hydroxide, and the lime salt formed filtered off. The filtrate was evaporated to a residue and the latter was extracted with strong alcohol, out of which the free betaine crystallised out. On recrystallising a purer preparation was obtained.

A further study will be made with the pure cotton seed, and of both the "Sea Island" and "Upland" varieties, in order to ascertain the comparative proportions of the nitrogenous bases present in the natural seed before it is subjected to expression of the oil and manufacture into cattle foods.

## ELECTROMOTIVE FORCE OF METALLIC SALTS.

BY C. L. SPEYERS.

*Copper.*

In continuation of a previous paper,<sup>1</sup> measurements of the electromotive force between copper and mercury in solutions of copper salts have been made, under my direction, in a most conscientious and able manner, by Mr. C. M. Hibbard, a senior student of the University.

For reasons previously stated, an amalgam was used, but, whereas a trifling addition of zinc to mercury gave it an electromotive force equal to that of zinc, a much larger amount of copper was required to effect a similar result. Most satisfaction was obtained by having pieces of amalgamated copper<sup>2</sup> floating in the amalgam; then the electromotive force of amalgam-mercury was sensibly equal to that of copper-mercury, provided no secondary action occurred, as evolution of hydrogen, formation of copper oxide, etc.; which secondary action, when not preventable, necessitated a replacement of the amalgam by a copper rod made of electrolytically deposited metal. This device does not do away with the thwarting action, but reduces its rapidity, for, when the amalgam was instantaneously affected, an appreciable time was required to corrode the copper surface. Amalgam measurements were made in the manner previously described, but the use of a rod involved a slight change in cell and manipulation. The mercury was contained in the tube, the stopper with its cup being replaced by a cork carrying the copper rod insulated by a glass tube. The deposit which formed on the rod was removed after each measurement by polishing with ground quartz and a clean rag, careful washing, and wiping with filter-paper. The liquids could be thoroughly mixed by shaking with a spiral motion.

Copper chloride was not available as an electrolyte, a film forming immediately upon the pure mercury, wherefore also all liquids containing this salt were excluded, as solutions of salts of copper and hydrochloric acid. Not so hydrochloric acid, alone or in combination with the other acids. The solutions were made by one of the methods previously described. To save space, only the mean increment,  $\Delta$ , is given. Temperature between  $20^{\circ}$  and  $25^{\circ}$ .

<sup>1</sup> This Journal 12, 254.

<sup>2</sup> The metal was obtained electrolytically.

$v$	$\frac{1}{2}\text{HCl.}$	$\frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{HAc.}^1$	$\frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HAc.}$
1	0.2564	0.3727	0.3595	0.3671	0.2524	0.2483
2	0.2437	0.4083	0.3590	0.3728	0.2252	0.2227
4	0.2288	0.4188	0.3586 <sup>2</sup>	0.3889	0.2061	0.2034
8	0.2122	0.4303 <sup>3</sup>	0.3586	0.3909	0.1978	0.1898
16	0.2287 <sup>2</sup>	0.4151	0.3546	0.3853	0.2074 <sup>6</sup>	0.1999 <sup>2</sup>
32	0.2363	0.4032	0.3595	0.3794	0.2282	0.2333
64	0.2391	0.3842	0.3534	0.3735	0.2350	0.2318
128	0.2390	0.3773	0.3506	0.3728	0.2356	0.2310
256	0.2354	.....	0.3440	0.3765 <sup>4</sup>	0.2208	0.2208
512	.....	.....	0.3393	0.3887	0.2291	0.2298
$\Delta = -0.0026 \quad \Delta = +0.0006 \quad \Delta = -0.0022 \quad \Delta = +0.0024 \quad \Delta = -0.0004 \quad \Delta = -0.0021$						

$v$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{HAc.}$	$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{HAc} + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{Cu(NO}_3)_2.$ <sup>1</sup>	$\frac{1}{2}\text{CuAc}_2.$ <sup>1</sup>
1	0.2379	0.3288	0.3695	0.3690	.....	.....
2	0.2174	0.3558	0.3853 <sup>7</sup>	0.3940	0.2316	0.1590
4	0.2000	0.3884	0.4035	0.4056 <sup>7</sup>	0.2370	0.1323
8	0.1845	0.4006	0.3990	0.4130	0.2258	0.1246
16	0.1610	0.4002	0.4151	0.4166	0.2366	0.1337
32	0.1600	0.4041	0.3916	0.4076	0.2207	0.1500 <sup>6</sup>
64	0.1612	0.3943	0.4088	0.4068	0.2165	0.1573
128	0.1831 <sup>6</sup>	0.3698	0.3823	0.3983	0.1925	0.1641
256	0.1985	0.3947	0.3810	0.4008	0.1841	0.1740
512	0.2142	0.3783	0.3780	0.3682	0.1690	.....
$\Delta = -0.0016 \quad \Delta = +0.0055 \quad \Delta = +0.0010 \quad \Delta = -0.0001 \quad \Delta = -0.0078 \quad \Delta = +0.0021$						

$v$	$\frac{1}{2}\text{CuSO}_4.$ <sup>1</sup>	$\frac{1}{2}\text{Cu(NO}_3)_2 + \frac{1}{2}\text{CuAc}_2.$ <sup>1</sup>	$\frac{1}{2}\text{Cu(NO}_3)_2 + \frac{1}{2}\text{CuSO}_4.$ <sup>1</sup>	$\frac{1}{2}\text{CuAc}_2 + \frac{1}{2}\text{CuSO}_4.$ <sup>1</sup>	$\frac{1}{2}\text{Cu(NO}_3)_2 + \frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{Cu(NO}_3)_2 + \text{HAc.}$
1	0.2531	.....	.....	.....	.....	.....
2	0.2659 <sup>9</sup>	0.1617 <sup>10</sup>	0.2422	0.1771	0.2715	0.2466
4	0.2737	0.1515	0.2530	0.1761	0.2913	0.2605
8	0.2721	0.1371	0.2592	0.1913	0.3092	0.2795
16	0.2675	0.1528	0.2592	0.2139	0.3203	0.2927 <sup>7</sup>
32	0.2630	0.1634	0.2550	0.2156	0.3311	0.3092
64	0.2569	0.1714	0.2440 <sup>9</sup>	0.2234	0.3419	0.3217
128	0.2440	0.1718	0.2400	0.2224	0.3403	0.3203
256	0.2345	0.1668	0.2374	0.2171	0.3528	0.3269
512	.....	.....	.....	0.2074 <sup>11</sup>	0.3364 <sup>7</sup>	.....
$\Delta = -0.0023 \quad \Delta = +0.0007 \quad \Delta = -0.0007 \quad \Delta = +0.0038 \quad \Delta = +0.0081 \quad \Delta = +0.0115$						

$v$	$\frac{1}{2}\text{Cu(NO}_3)_2 + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{CuAc}_2 + \frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{CuAc}_2 + \frac{1}{2}\text{HAc.}^1$	$\frac{1}{2}\text{CuAc}_2 + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{CuSO}_4 + \frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{CuSO}_4 + \frac{1}{2}\text{HAc}$
1	.....	.....	.....	.....	0.2745	0.2592 <sup>5</sup>
2	0.2791	0.2339	0.2037	0.2552	0.3086	0.2715
4	0.3067	0.2523	0.2099	0.2801	0.3234	0.2812
8	0.3247	0.2760	0.2214	0.3000 <sup>11</sup>	0.3347	0.3027
16	0.3388	0.2966	0.2353 <sup>7</sup>	0.3000	0.3466	0.3020
32	0.3476 <sup>11</sup>	0.3135 <sup>5</sup>	0.2410	0.3184	0.3540	0.3176
64	0.3604	0.3194	0.2586	0.3299	0.3604 <sup>10</sup>	0.3277
128	0.3795	0.3212	0.2656	0.3306	0.3643	0.3335 <sup>7</sup>
256	0.3687	0.3192	0.2809	0.3310	0.3683	0.3363
512	0.3698	.....	0.2914	0.3298	0.3679	.....
$\Delta = +0.0113 \quad \Delta = +0.0122 \quad \Delta = +0.0109 \quad \Delta = +0.0093 \quad \Delta = +0.0104 \quad \Delta = +0.0097$						

<sup>1</sup> Copper rod in place of amalgam.<sup>2</sup> 9 per cent. from mean.<sup>3</sup> 7 per cent. from mean.<sup>4</sup> 8 per cent. from mean.<sup>6</sup> 5 " " "<sup>6</sup> 13 " " "<sup>7</sup> 2 " " "<sup>8</sup> 14 " " "<sup>9</sup> 4 " " "<sup>10</sup> 6 " " "<sup>11</sup> 3 " " "

2 <sup>1</sup>	$\frac{1}{2}\text{CuSO}_4 + \frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{2}\text{ZnCl}_2$	$\frac{1}{2}\text{Zn}(\text{NO}_3)_2$	$\frac{1}{2}\text{ZnAc}_2$ <sup>1</sup>	$\frac{1}{2}\text{ZnSO}_4$ <sup>1</sup>	
1	0.3155	0.2489	0.3005	.....	0.2662	
2	0.3236	0.2482	0.3133	0.2565	0.2596	
4	0.3290	0.2194	0.3337	0.2608	0.2546	
8	0.3325	0.2073	0.3451	0.2652	0.2492	
16	0.3540	0.2103	0.3236 <sup>2</sup>	0.2549	0.2448	
32	0.3608	.....	.....	0.2487	0.2347	
64	0.3656	.....	.....	0.2440	0.2199	
128	0.3654	.....	.....	0.2296 <sup>3</sup>	0.2078	
256	0.3707	.....	.....	0.2039	0.1991	
512	0.3559	.....	.....	0.1950	0.1957	
	$\Delta = +0.0045$	$\Delta = -0.0095$	$\Delta = +0.0058$	$\Delta = -0.0077$	$\Delta = -0.0078$	

Owing to tarnishing, these measurements are by no means so accurate as those with zinc. Judgment, sometimes rather arbitrary, was necessary, but fairly consistent results were obtained by taking the value immediately after the first rapid rise, before the rod had time to tarnish. When the rise was followed by a fall the highest value was recorded, for thereby most consistent results could be obtained. Whenever the deviation of either of a pair of measurements exceeded one per cent. of their mean, the determination was repeated and the average of four measurements given, with their maximum deviation added in a foot-note. In some cases this is very large, for the disturbing effect of oxidation is probably as great here as in the preceding zinc measurements, but the basis of calculation is much smaller. Notwithstanding we can readily perceive that:

1. The average increment is usually small; whenever large it is positive, except with copper nitrate and zinc chloride, acetate, and sulphate. But owing to the small initial value, dilution from  $\frac{1}{2}$  equivalent to  $\frac{1}{512}$  equivalent can increase the electromotive force over 43 per cent. ( $\frac{1}{2}\text{CuAc}_2 + \frac{1}{512}\text{HAc}$ ), or with the amalgam, over 36 per cent. when diluted to  $\frac{1}{256}$  equivalent ( $\frac{1}{2}\text{CuAc}_2 + \frac{1}{256}\text{HNO}_3$ ).

2. The electromotive force in hydrochloric acid is lower than in the other three acids which form a group by themselves, the somewhat low value of acetic acid being doubtless connected with the use of the rod, for in its acid mixtures this acid acts like nitric and sulphuric acids.

3. The electromotive force in mixtures containing hydrochloric acid is the same or less, never markedly greater, than in hydrochloric acid alone. The other acids having an electromotive force nearly equal, their mixtures indicate little.

<sup>1</sup> Copper rod in place of amalgam.<sup>2</sup> 2 per cent. from mean.<sup>3</sup> 4 per cent. from mean.

4. Substitution of copper for hydrogen lowers the electromotive force very much, but excessive secondary action forbids numerical comparison.

5. In mixed solutions of two salts of different metallic and acid radicles, the electromotive force is only slightly greater than in the solution having the lower value, due consideration being taken of the weak nature of acetic acid.

6. The electromotive force in  $\frac{1}{2}\text{CuR} + \text{HR}'$  is sensibly the same as in  $\frac{1}{2}\text{CuR}' + \text{HR}$ , the difference in concentrated solutions disappearing on dilution.

### Iron.

An iron amalgam not being readily obtainable, the metal, as pianoforte wire, was arranged in a cork and the measurements performed exactly as with copper, and for a corresponding reason measurements in ferric chloride had to be omitted. Whenever the deviation from the mean was sensibly over one per cent., four measurements were made.

$v$	$\frac{1}{2}\text{HCl.}$	$\frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{HAc.}$	$\frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{HAc.}$	$\frac{1}{2}\text{HCl} + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{HAc.}$
1	0.5055	0.6992	0.8355 <sup>2</sup>	0.8023 <sup>2</sup>	0.4643 <sup>3</sup>	0.5287	0.5113	0.6655
2	0.5227	0.7401	0.8399	0.8221	0.4717	0.5386	0.5238	0.6761
4	0.5415	0.7767	0.8411	0.8340	0.4873	0.5559	0.5547	0.7150
8	0.5734	0.8179	0.8673	0.8511	0.5699	0.5815	0.5847	0.7554
16	0.6013	0.8523	0.8829	0.8639	0.6249	0.6078	0.6184	0.8094
32	0.6231	0.8939 <sup>1</sup>	0.8990	0.8748	0.6731	0.6395	0.6474	0.8600
64	0.6575	0.9257	0.9207	0.8902	0.7189	0.6701	0.6778	0.9076
128	0.6901	0.9479	0.9466	0.9068	0.7604	0.7107	0.7113	0.9430
256	0.7185	0.9548	0.9753	0.9659	0.8088	0.7961 <sup>3</sup>	0.7655	0.9633
512	0.8241	0.9673	0.9855	1.0192	0.8504	0.8754	0.8441	0.9736
	$\Delta = 0.0354$	$\Delta = 0.0298$	$\Delta = 0.0167$	$\Delta = 0.0241$	$\Delta = 0.0429$	$\Delta = 0.0385$	$\Delta = 0.0370$	$\Delta = 0.0342$

$v$	$\frac{1}{2}\text{HNO}_3 + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{HAc} + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{3}\text{Fe}(\text{NO}_3)_3.$	$\frac{1}{3}\text{FeAc}_3.$	$\frac{1}{6}\text{Fe}_2(\text{SO}_4)_3.$	$\frac{1}{3}\text{Fe}(\text{NO}_3)_3 + \frac{1}{3}\text{FeAc}_3.$	$\frac{1}{3}\text{Fe}_3(\text{NO}_4)_2 + \frac{1}{6}\text{Fe}(\text{SO}_3)_4.$
1	0.7087 <sup>4</sup>	0.7800	.....	.....	0.9219	.....	.....
2	0.7352	0.8153	0.9323	0.8177	0.9391	0.8635	0.9346
4	0.7550	0.8327	0.9508	0.8826	0.9592	0.8910	0.9684
8	0.8092	0.8456	0.9108	0.8967	0.9723	0.9121	0.9959
16	0.8178	0.8603 <sup>2</sup>	0.9601 <sup>2</sup>	0.9059	0.9884	0.9455	1.0244
32	0.8764	0.8763	0.9607	0.9211	1.0010	0.9711 <sup>2</sup>	1.0342
64	0.9114	0.8947	0.9809	0.9405	1.0322	0.9947	1.0485
128	0.9356	0.9160	1.0028	0.9785	1.0456	1.0011	1.0586
256	0.9792	0.9613	1.0112	1.0085	1.0395	1.0187	1.0695
512	0.9782	1.0237	1.0039	0.9592 <sup>4</sup>	1.0610 <sup>5</sup>	1.0100	1.0717
	$\Delta = 0.0300$	$\Delta = 0.0271$	$\Delta = 0.0089$	$\Delta = 0.0177$	$\Delta = 0.0154$	$\Delta = 0.0194$	$\Delta = 0.0171$

<sup>1</sup> 3 per cent. from mean.<sup>2</sup> 2 per cent. from mean.<sup>3</sup> 8 per cent. from mean.<sup>4</sup> 4 per cent. from mean.<sup>5</sup> 5 per cent. from mean.



$\nu$	$\frac{1}{3}\text{FeAc}_3 + \frac{1}{6}\text{Fe}_2(\text{SO}_4)_3$	$\frac{1}{3}\text{Fe}(\text{NO}_3)_3 + \frac{1}{1}\text{HNO}_3$	$\frac{1}{3}\text{Fe}(\text{NO}_3)_3 + \frac{1}{1}\text{HAc}$	$\frac{1}{3}\text{Fe}(\text{NO}_3)_3 + \frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{3}\text{FeAc}_3 + \frac{1}{1}\text{HNO}_3$	$\frac{1}{3}\text{FeAc}_3 + \frac{1}{1}\text{HAc}$
1	.....	.....	.....	.....	.....	.....
2	0.9443	0.8784	0.8411	0.8744	0.7855	0.8633
4	0.9498	0.9135	0.8678 <sup>1</sup>	0.9144	0.8249	0.8875
8	0.9600	0.9460	0.8925	0.9460	0.8524	0.8961
16	0.9691	0.9662	0.9177	0.9734	0.8835	0.9078
32	0.9791	0.9666	0.9503	1.0248	0.9303	0.9176
64	0.9963	0.9798	0.9833	1.0200	0.9533	0.9358
128	1.0122	0.9922	0.9956	1.0280	0.9727 <sup>1</sup>	0.9675
256	1.0571	1.0106	1.0131	1.0444	0.9838	1.0040
512	1.0765	1.0325	1.0120	1.0597	1.0027	0.9782
	$\Delta = 0.0165$	$\Delta = 0.0193$	$\Delta = 0.0214$	$\Delta = 0.0222$	$\Delta = 0.0217$	$\Delta = 0.0144$

$\nu$	$\frac{1}{3}\text{FeAc}_3 + \frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{6}\text{Fe}_2(\text{SO}_4)_3 + \frac{1}{1}\text{HNO}_3$	$\frac{1}{6}\text{Fe}_2(\text{SO}_4)_3 + \frac{1}{1}\text{HAc}$	$\frac{1}{6}\text{Fe}_2(\text{SO}_4)_3 + \frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{2}\text{FeCl}_2$	$\frac{1}{2}\text{Fe}(\text{NO}_3)_2$
1	.....	0.8309	0.9170	0.8900	.....	.....
2	0.9104	0.8754	0.9329	0.9074	0.6678	.....
4	0.9210	0.9150	0.9495	0.9289	0.6892	0.7079
8	0.9349	0.9390	0.9632	0.9475	0.7061	0.7340
16	0.9472	0.9727	0.9770	0.9610	0.6184	0.6410
32	0.9600	1.0012	0.9943	0.9707	0.6184	0.6074
64	0.9728	1.0205	1.0070	0.9775	0.6160 <sup>2</sup>	0.6049
128	0.9912 <sup>1</sup>	1.0362	1.0099	0.9945	0.6488	0.5883
256	1.0227	1.0419	1.0451	1.0058	0.6362	0.5938
512	1.0670	1.0684	1.0570	1.0339	.....	0.5904 <sup>3</sup>
	$\Delta = 0.0196$	$\Delta = 0.0264$	$\Delta = 0.0156$	$\Delta = 0.0160$	$\Delta = 0.0045$	$\Delta = 0.0296$

$\nu$	$\frac{1}{2}\text{FeAc}_2$	$\frac{1}{2}\text{FeSO}_4$	$\frac{1}{2}\text{FeCl}_2 + \frac{1}{1}\text{HCl}$	$\frac{1}{2}\text{FeCl}_2 + \frac{1}{1}\text{HNO}_3$	$\frac{1}{2}\text{FeCl}_2 + \frac{1}{1}\text{HAc}$	$\frac{1}{2}\text{FeCl}_2 + \frac{1}{2}\text{H}_2\text{SO}_4$
1	.....	0.8719	0.5165	0.4690 <sup>1</sup>	.....	.....
2	0.4528	0.9013	0.5255	0.4681	0.5908	0.5537
4	0.5375	0.9152	0.5421	0.5305	0.6224	0.5710
8	0.5347	0.8567	0.5724	0.6005	0.6545	0.5942
16	0.6225 <sup>3</sup>	0.8017	0.5957	0.6460	0.6822	0.6203
32	0.6918	0.7376	0.6277	0.7006	0.7147	0.6572
64	0.7312	0.7424	0.6678	0.7420	0.7639	0.6897
128	0.8192	0.6910 <sup>4</sup>	0.7025	0.7700	0.8089 <sup>5</sup>	0.7296
256	.....	0.6327	0.7630	0.8061	0.8459	0.7732
512	.....	0.6020	0.8474	.....	0.6927	0.8549 <sup>6</sup>
	$\Delta = 0.0611$	$\Delta = 0.0300$	$\Delta = 0.0368$	$\Delta = 0.0421$	$\Delta = 0.0127$	$\Delta = 0.0377$

$\nu$	$\frac{1}{2}\text{Fe}(\text{NO}_3)_2 + \frac{1}{1}\text{HCl}$	$\frac{1}{2}\text{Fe}(\text{NO}_3)_2 + \frac{1}{1}\text{HNO}_3$	$\frac{1}{2}\text{Fe}(\text{NO}_3)_2 + \frac{1}{1}\text{HAc}$	$\frac{1}{2}\text{Fe}(\text{NO}_3)_2 + \frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{2}\text{FeAc}_2 + \frac{1}{1}\text{HCl}$	$\frac{1}{2}\text{FeAc}_2 + \frac{1}{1}\text{HNO}_3$
1	.....	.....	.....	.....	.....	.....
2	.....	.....	.....	.....	0.6181	0.7277
4	0.5272	0.7454	0.7495	0.7224 <sup>1</sup>	0.6340	0.7621
8	0.6064	0.8102	0.7857	0.7892	0.6565	0.8014
16	0.6592 <sup>5</sup>	0.8007	0.8258	0.8296	0.6931	0.8415
32	0.6995	0.8936	0.8605	0.8648	0.7236	0.8843
64	0.7304	0.9209	0.8894	0.8994	0.7638	0.9037
128	0.7719	0.9363	0.9073	0.9265	0.8239	0.9251
256	0.8036	0.9514	0.9232	0.9186	0.8784	0.9322
512	0.8368	0.9441 <sup>7</sup>	0.7387 <sup>3</sup>	0.9679	0.7229 <sup>8</sup>	0.7658 <sup>7</sup>
	$\Delta = 0.0442$	$\Delta = 0.0284$	$\Delta = 0.0015$	$\Delta = 0.0351$	$\Delta = 0.0136$	$\Delta = 0.0048$

<sup>1</sup> 2 per cent. from mean.<sup>2</sup> 4 per cent. from mean.<sup>3</sup> 10 per cent. from mean.

4 6 " " "

5 3 " " "

6 8 " " "

7 5 " " "

8 7 " " "

<i>N</i>	$\frac{1}{2}\text{FeAc}_2 + \frac{1}{2}\text{HAc.}$	$\frac{1}{2}\text{FeAc}_2 + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{FeSO}_4 + \frac{1}{2}\text{HCl.}$	$\frac{1}{2}\text{FeSO}_4 + \frac{1}{2}\text{HNO}_3.$	$\frac{1}{2}\text{FeSO}_4 + \frac{1}{2}\text{HAc.}$	$\frac{1}{2}\text{FeSO}_4 + \frac{1}{2}\text{H}_2\text{SO}_4.$
1	.....	.....	0.5277	0.6911	0.7243	0.7595
2	0.6147	0.7871	0.5444	0.7414 <sup>4</sup>	0.7435	0.7683
4	0.6632	0.8052	0.5649	0.7847	0.7687	0.7802
8	0.7063	0.8225	0.5944	0.8233	0.7933	0.8019
16	0.7591	0.8393	0.6235	0.8583	0.8143	0.8209
32	0.8031	0.8654	0.6550	0.8888	0.8446	0.8454
64	0.8651	0.8966	0.6872	0.9096	0.8735	0.8659
128	0.8930	0.9333	0.7200 <sup>3</sup>	0.9301	0.9072	0.9165
256	0.9233	0.9601	0.7644	0.9557	0.9364	0.9457 <sup>3</sup>
512	0.641 <sup>1</sup>	0.7709 <sup>2</sup>	0.8466	0.9746	0.7837	1.0035
	$\Delta = 0.0087$	$\Delta = -0.0020$	$\Delta = 0.0354$	$\Delta = 0.0315$	$\Delta = 0.0066$	$\Delta = 0.0281$

<i>N</i>	$\frac{1}{2}\text{FeSO}_4 + \frac{1}{3}\text{FeAc}_3.$	$\frac{1}{2}\text{FeSO}_4 + \frac{1}{6}\text{Fe}_2(\text{SO}_4)_3.$	$\frac{1}{2}\text{ZnCl}_2.$	$\frac{1}{2}\text{Zn}(\text{NO}_3)_2.$	$\frac{1}{2}\text{ZnAc}_2.$	$\frac{1}{2}\text{ZnSO}_4.$
1	.....	0.8843	0.5795	0.7794	.....	0.8035
2	0.7537	0.9134	0.6171	0.8081	0.7568	0.8153
4	0.7727	0.9432	0.5742	0.8266	0.6876	0.8352
8	0.7811	0.9540	0.5774	0.8164 <sup>4</sup>	0.6000 <sup>7</sup>	0.8383
16	0.8101	0.9773	0.5970	0.6732	0.4790	0.8407
32	0.8381	1.0043	0.5920	0.6160	0.4692	0.8114
64	0.8546	1.0232	0.5381 <sup>6</sup>	0.5716	0.4719	0.7720
128	0.8951	1.0420	0.5276	0.5318	0.4849	0.7276
256	0.8057	1.0629	0.5521	0.5310	0.4975	0.7669
512	0.6741 <sup>4</sup>	0.9342 <sup>5</sup>	.....	0.5237	0.4924	0.7352 <sup>6</sup>
	$\Delta = -0.0099$	$\Delta = -0.0055$	$\Delta = -0.0034$	$\Delta = -0.0284$	$\Delta = -0.0330$	$\Delta = -0.0076$

Bearing in mind the uncertainty due to tarnishing—an uncertainty much less in most cases than with copper, both in percentage and in absolute value—it will be seen that :

1. The electromotive force always increases on dilution, except in solutions of the pure ferrous and zinc salts. Curious in behavior are solutions containing ferrous acetate, for the electromotive force rises in the usual manner to the 10th dilution, when a drop of from 140 to 240 millivolts occurs. Unfortunately, solutions of pure ferrous acetate decomposed so rapidly that beyond the 8th dilution no reliable measurements were obtainable. The result of this drop is to make the increment sometimes negative, but these cases are evidently different in nature from those in which it is negative throughout.

2. The electromotive force in hydrochloric acid is lower than in the other three acids, which again form a group by themselves, with nitric acid the lowest.

3. The electromotive force in equivalent mixtures containing hydrochloric acid equals or is less, never markedly greater, than

<sup>1</sup> 10 per cent. from mean.

<sup>4</sup> 2 " " "

<sup>2</sup> 8 per cent. from mean.

<sup>5</sup> 4 " " "

<sup>7</sup> 23 " " "

<sup>3</sup> 3 per cent. from mean.

<sup>6</sup> 15 " " "

that in hydrochloric acid alone. The other acids have an electromotive force so nearly equal that an equivalent statement cannot be demonstrated in their mixtures, yet it appears that the influence of that acid predominates in which the electromotive force is lowest. For in mixtures of nitric acid with acetic and sulphuric acids it is appreciably lower than in a mixture of the last two.

### *Ferric Salts.*

4. Substitution of iron for hydrogen apparently raises the electromotive force, but the excessive secondary action, tarnishing of wire or mercury or decomposition of liquid, makes numerical comparison illusory.

5. In mixed solutions of two salts of different metallic and acid radicles, the electromotive force shows no regular dependence upon the constituents.

6. The electromotive force in  $\frac{1}{3}\text{FeR}_3 + \frac{1}{3}\text{HR}'$  is not always equal to that in  $\frac{1}{3}\text{FeR}'_3 + \frac{1}{3}\text{HR}$ , especially in  $\frac{1}{3}\text{Fe}(\text{NO}_3)_3 + \frac{1}{3}\text{HAc}$  and  $\frac{1}{3}\text{FeAc}_3 + \frac{1}{3}\text{HNO}_3$ . However, the color of the two mixtures showed that their constituents were not the same, but after heating for a couple of days to about  $100^\circ$  they were indistinguishable in color and electromotive force. Similarly with  $\frac{1}{3}\text{Fe}_2(\text{SO}_4)_3 + \frac{1}{3}\text{HAc}$  and  $\frac{1}{3}\text{FeAc}_3 + \frac{1}{3}\text{H}_2\text{SO}_4$ .

### *Ferrous Salts.*

4. The introduction of iron increases the electromotive force in three cases, but in the fourth diminishes it. However, in the latter the increment is strongly positive, while more or less negative in the other three, indicating a difference in the action of ferrous acetate on the one hand, and ferrous chloride, nitrate, and sulphate on the other. Moreover, the low electromotive force in the acetate is raised by the addition of acetic acid, so that when compared with the other ferrous salts correspondingly treated, the acetate assumes its proper position, and the chloride has the smallest value.

5. The electromotive force is lowest in solutions containing chlorine, excepting the ferrous acetate solution.

6. The electromotive force of  $\frac{1}{2}\text{FeR} + \text{HR}'$  is equal to  $\frac{1}{2}\text{FeR}' + \text{HR}$ , when R is chlorine; otherwise the agreement is unsatisfactory, as in solutions of ferric salts.

*Tin.*

An amalgam was used in most of these measurements, the exceptions being noted. Tarnishing occurred only in nitric acid and in solutions of ferric sulphate and nitrate, but so violently in the last, that no value can be attached to the measurements in it. The tin rod substituted for the amalgam was treated in the same manner as the iron wire.

<i>v</i>	$\frac{1}{1}\text{HCl.}$	$\frac{1}{1}\text{HNO}_3.$	$\frac{1}{1}\text{HAc.}$	$\frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{1}\text{HCl} + \frac{1}{1}\text{HNO}_3.$	$\frac{1}{1}\text{HCl} + \frac{1}{1}\text{HAc.}$
1	0.5840	0.8228	0.8467	0.8211	0.5860	0.5880
2	0.5880	0.7810 <sup>1</sup>	0.8364 <sup>2</sup>	0.8123	0.5994	0.5908
4	0.5864	0.7333	0.8015	0.8148	0.5834	0.6060
8	0.5946	0.7080	0.7911	0.7979	0.5998	0.6083
16	0.6127	0.7061	0.7876	0.7905	0.6272	0.6233
32	0.6250	0.6936	0.7838	0.7514 <sup>1</sup>	0.6386	0.6350
64	0.6363	0.6690	0.7888	0.7234	0.6518	0.6465
128	0.6508	0.6488	0.8075	0.7079	0.6671	0.6699
256	0.6734	0.6690	0.8084	0.7056	0.6890	0.6947
512	0.6947	0.6936	0.8229	0.7008	0.7077	0.7223
	$\Delta = 0.0123$	$\Delta = -0.0144$	$\Delta = -0.0026$	$\Delta = -0.0134$	$\Delta = 0.0135$	$\Delta = 0.0149$

<i>v</i>	$\frac{1}{1}\text{HCl} + \frac{1}{2}\text{H}_2\text{SO}_4.$	$\frac{1}{4}\text{SnCl}_4.$	$\frac{1}{4}\text{SnCl}_4 + \frac{1}{1}\text{HCl.}$	$\frac{1}{4}\text{SnCl}_4 + \frac{1}{1}\text{HNO}_3.$	$\frac{1}{4}\text{SnCl}_4 + \frac{1}{1}\text{HAc.}$	$\frac{1}{4}\text{SnCl}_4 + \frac{1}{2}\text{H}_2\text{SO}_4.$
1	0.5975	0.5739	0.5760	0.5827	0.6022	0.5940
2	0.6032	0.5996	0.5956	0.5974	0.6150	0.5978
4	0.5891	0.6153	0.6117	0.6131	0.6244	0.6236
8	0.6119	0.6290	0.6207	0.6274	0.6304	0.6578
16	0.6344	0.6308	0.6197	0.6286	0.6423	0.6732
32	0.6488	0.6365	0.6292	0.6399	0.6530	0.6887
64	0.6602	0.6473	0.6456	0.6581	0.6625	0.6979
128	0.6791	0.6647	0.6572	0.6771	0.6773	0.7089
256	0.6977	0.6770	0.6752	0.6877	0.7067	0.7195
512	0.7181	0.7059	0.7046	0.7183	0.7472	0.7412
	$\Delta = 0.0134$	$\Delta = 0.0147$	$\Delta = 0.0154$	$\Delta = 0.0153$	$\Delta = 0.0161$	$\Delta = 0.0164$

<i>v</i>	$\frac{1}{2}\text{SnCl}_2.$ <sup>8</sup>	$\frac{1}{2}\text{SnCl}_2 + \text{HCl.}$	$\frac{1}{2}\text{SnCl}_2 + \text{HNO}_3.$	$\frac{1}{2}\text{SnCl}_2 + \frac{1}{2}\text{HAc.}$	$\frac{1}{2}\text{SnCl}_2 + \frac{1}{1}\text{H}_2\text{SO}_4.$	$\frac{1}{2}\text{ZnCl}_2.$
1	0.2883	0.3511	0.3990	0.3105	0.3743	0.6330
2	0.2945	0.3837 <sup>4</sup>	0.3919	0.3000	0.3750	0.6734
4	0.2932	0.3796	0.3694	0.2933	0.3594	0.6947
8	0.2644	0.3525	0.3633	0.2926	0.3453	0.7123
16	0.2653	0.3446	0.4333 <sup>5</sup>	0.3994 <sup>6</sup>	0.3380	0.7149
32	0.2335	0.3463	0.5252	0.4338	0.3781	0.7270
64	0.2000	0.5109	0.5231	0.5056	0.4783 <sup>7</sup>	0.7411
128	0.1900	0.5237	0.5328	0.4976	0.5327	0.7554
256	0.5184 <sup>8</sup>	0.5227	0.5303	0.4958	0.5360	0.7768
512	0.5181	0.5637	0.5462	0.5175	0.5828	0.8018
	$\Delta = 0.0255$	$\Delta = 0.0236$	$\Delta = 0.0164$	$\Delta = 0.0230$	$\Delta = 0.0232$	$\Delta = 0.0188$

<sup>1</sup> 3 per cent. from mean.<sup>2</sup> 5 per cent. from mean.<sup>3</sup> 2 per cent. from mean.<sup>4</sup> 7 " " "<sup>5</sup> 17 " " "<sup>6</sup> 35 " " "<sup>7</sup> 23 " " "<sup>8</sup> Tin rod.

<i>v</i>	$\frac{1}{2}\text{Zn}(\text{NO}_3)_2$	$\frac{1}{3}\text{ZnAc}_2$	$\frac{1}{2}\text{ZnSO}_4$	$\frac{1}{3}\text{Fe}(\text{NO}_3)_3$ <sup>3</sup>	$\frac{1}{3}\text{FeAc}_3$ <sup>3</sup>	$\frac{1}{6}\text{Fe}_2(\text{SO}_4)_3$ <sup>3</sup>
1	0.6878	.....	0.8176	.....	.....	0.8949
2	0.6744 <sup>1</sup>	0.8078	0.8221	0.8660	0.8869	0.9094
4	0.6796	0.8135 <sup>2</sup>	0.8174	0.8559	0.8771	0.9090
8	0.6741	0.8016	0.8209	0.8559	0.8516	0.9044
16	0.7180	0.8161	0.8236	0.8458	0.8358	0.9044
32	0.7626	0.8213	0.8205	0.8053	0.8278	0.8958
64	0.7991	0.8310	0.8127	0.7666	0.8145	0.8913
128	0.8073	0.8217	0.8085	0.7666	0.8154	0.8611
256	0.8106	0.8279	0.8027	0.7666	0.8175	0.8521
512	0.8127	0.8218	0.8056	0.8154	0.8177	0.8254
	$\Delta = 0.0139$	$\Delta = 0.0018$	$\Delta = -0.0013$	$\Delta = -0.0063$	$\Delta = -0.0087$	$\Delta = -0.0077$

1. The electromotive force rises in general on dilution; in nitric and sulphuric acids, however, the increment is markedly negative. In the first case the amalgam tarnished when left in the liquid for some time, to avoid which the values had to be recorded, while still increasing, though very slowly, and in the second case the same was done to avoid tarnishing. In acetic acid the negative increment is very slight; both it and the somewhat larger numerical values in the iron solutions can be explained by a secondary action which was proven to exist in the solution of ferric acetate. A very curious occurrence is to be noted in solutions of stannous chloride, alone and with acids, a proceeding the reverse of that in ferrous acetate, for the electromotive force decreases to the 5th-9th dilution, when a sudden rise occurs. This is possibly due to formation of stannic salts; yet the solution of stannous chloride and nitric acid gave a precipitate with mercuric chloride at the 9th dilution. The 10th dilution of this liquid was not tested, but a solution of stannous chloride and acetic acid at this dilution gave a precipitate, proving in both cases the presence of stannous, though not the absence of stannic salt.

2. The electromotive force in hydrochloric acid is much lower than in the other acids, which latter form a group by themselves.

3. In mixtures of hydrochloric acid with other acids the electromotive force is the same as that in hydrochloric acid.

4. Substitution of stannic tin for hydrogen hardly changes the electromotive force, but substitution of stannous tin lowers it very much.

5. In mixtures of salts containing different metallic and acid radicles the electromotive force is determined by the constituent having the lower value.

<sup>1</sup> 3 per cent. from mean.<sup>2</sup> 4 per cent. from mean.<sup>3</sup> Tin rod.



Finally, the large deviations in the tables—15 to 35 per cent.—would mislead were the matter left unexplained. The aberrations occur where there is a rapid rise or fall and where the measurements have been made four times. Of these four, one generally takes the jump before the others, and therefore causes the wide departure from the mean, though before and after the jump all is regular.

The foregoing, taken collectively, clearly indicates the probability that the electromotive force is increased by dilution, even if it does not prove it. Is an explanation of this supposed law to be found in the dissociation or, better, *ionisation* hypothesis?—an hypothesis that asserts that a metallic salt in solution is partially separated into its ions, and that dilution increases the quantity thus separated or ionised, so that in a dilute solution no ions exist in combination. As yet no satisfactory explanation has been deduced. Ionisation increasing with dilution, the mean free path of each ion is lengthened; wherefore each atom, positive as well as negative, is less under the influence of the other, and appears, therefore, to impart more electricity to its electrode—to raise it to a higher potential. But this is hardly more than a statement of the above results in other words.

On the other hand, the ionisation hypothesis readily explains the production of electricity.<sup>1</sup> On introducing a metal into an electrolyte—an acid, for instance—both ions, in this case hydrogen and the acid radicle, will strike the metal. The negative ion will attract positive electricity, repelling negative, and go off with the metal in chemical combination, while the positive hydrogen ion will attract negative electricity, repelling positive, and thereby become neutral. But this does not continue indefinitely, nor until the metal is dissolved, for two reasons: first, the accumulated negative electricity gradually repels the negative ion, and finally altogether forbids its contact with the metal; secondly, the more negative the metal becomes the more hydrogen it attracts, which, accumulating on the surface, effectually shuts out the negative ion. The first is auxiliary rather than essential, for it is probable that before negative electricity could accumulate sufficiently altogether to repel the negative ions it would be carried off by the liquid, for a piece of gold leaf thrown into an aqueous solution of chlorine readily dissolves. The second, however, is very effective in bring-

<sup>1</sup> See Sohnke: *Ztschr. phys. Chem.* **3**, 1.

ing matters to a standstill. On introducing a second metal into the acid a similar process occurs, but not to the same extent, for there is cumulative evidence that elements differ in their relations to electricity, each allowing it to pass, but with diverse facility. So soon as electrical connection is established the potential of the two electrodes is equalised, and therefore diminished on one electrode and increased on the other. The result is that the negative ion which was in equilibrium with the electrode of lower negative potential is repelled, as the negative potential is increased, toward the electrode at first of higher negative potential, where also the equilibrium being disturbed by a reduction of negative potential, negative ions can again approach. At the same time the attraction for hydrogen is diminished, but is increased at the other electrode by the higher negative potential, and consequently hydrogen collects here. So long as electrical communication is kept up this state of things is continuously renewed, and a current produced and maintained by the partial discharge of the hydrogen ions and carrying off of electricity by the negative ions with the metal.

We shall assume that the positive and negative ions act very differently upon electricity, and by pushing this assumption we may reach a somewhat reasonable explanation of chemical affinity based upon the non-conductivity of the "non-metals" and the well known mutual attraction of positive and negative electricities. To do so we premise that the total quantity of electricity contained *within*<sup>1</sup> any given mass of an element is constant (possibly it may vary as the equivalence, but for the present this is to be left undecided); that in metals and other good conductors this electricity may be all positive electricity, or positive and negative. When these are present in equal quantities the atom is neutral. The non-metals are non-conductors and contain negative electricity. Their atoms are like spheres surrounded by an insulating shell within which is one or more charges of negative electricity. When such an atom comes in contact with a metal the positive electricity is attracted, the negative repelled; but as the electricities cannot unite owing to the insulation of the negative ion, a quantity of matter containing the same number of unit-charges of *positive* electricity is carried off with it in so-called "chemical combination." Wherefore, the better the

<sup>1</sup> This excludes any artificial charge to be found on the surface.

insulation of the negative ion and the less negative electricity in the positive ion, the more firmly<sup>1</sup> are the ions chemically united. In accordance herewith combinations of metals should be weak; likewise those of non-metals, owing to the presence of negative electricity. But a combination of a non-conductor or insulator with an excellent conductor should be strong, and this idea experience confirms.

The separation of this electricity consumes energy and, as indicated in a previous paper, we might expect to find the chemical energy, as measured by heat, equal to that consumed in the separation. In order that this equality may exist the performance of other internal work is impossible; but as internal work generally exists, the equality is exceptional. Helmholtz has indeed demonstrated the matter, though not in this form. By thermodynamical manipulation he has shown<sup>2</sup> that whenever the electromotive force is a function of temperature the two energies in question are not equal, but that the relation between heat ( $Q$ ), internal energy ( $U$ ), temperature ( $T$ ), electromotive force ( $p$ ), and quantity of electricity ( $e$ ), is

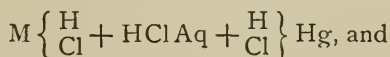
$$dQ = \frac{\partial U}{\partial T} dT + \frac{\partial p}{\partial T} de.$$

Yet since this demonstration requires the aid of the second law of thermodynamics,

$$\int \frac{dQ}{T} = 0,$$

the first equation is only strictly applicable to reversible cells; however, the principle involved therein, that the internal energy must be considered, is of universal application. Hence the futility in expecting to find the chemical and electrical energies numerically equal, and this is well shown by a comparison, so far as thermal data will permit, of the calculated and observed electromotive forces of zinc, copper, iron, tin and mercury in solutions of hydrochloric and nitric acids.

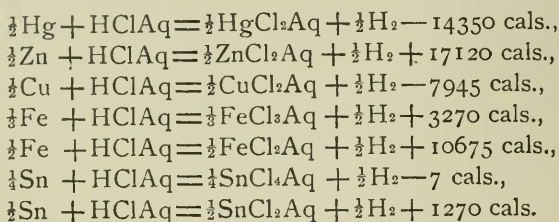
If the electrodes are electrically disconnected we have



<sup>1</sup> Used in the ordinary sense.

<sup>2</sup> Gesammelte Abhandlungen 2, 961.

Accordingly, each electrode tending to produce a current in opposite directions, the difference of the chemical energies is to be taken as the measure of electromotive force. We have from Thomsen's data:<sup>1</sup>



The energy-equivalent of one calorie is  $4153 \cdot 10^4$  c. g. s. units; hence the energy ( $W$ ) of the above reactions is

$$W = \text{cals. } 4153 \cdot 10^4.$$

Now as one unit of electricity, or one coulomb, is contained in 0.001118 gram of silver, one gram-equivalent of this metal or any other substance contains

$$0.001118 \cdot 107.94 = 96540 \text{ coulombs.}$$

The energy consumed in producing this quantity of electricity is determined by its electric height, or electromotive force, that is,

$$W = 96540 \cdot EF = EF \cdot 9654 \text{ c. g. s. units.}$$

On combination with the above equation,

$$EF = \frac{\text{cals. } 4153 \cdot 10^4}{9654 \cdot 10^3} = \text{cals. } 4302 \cdot 10^{-8}.$$

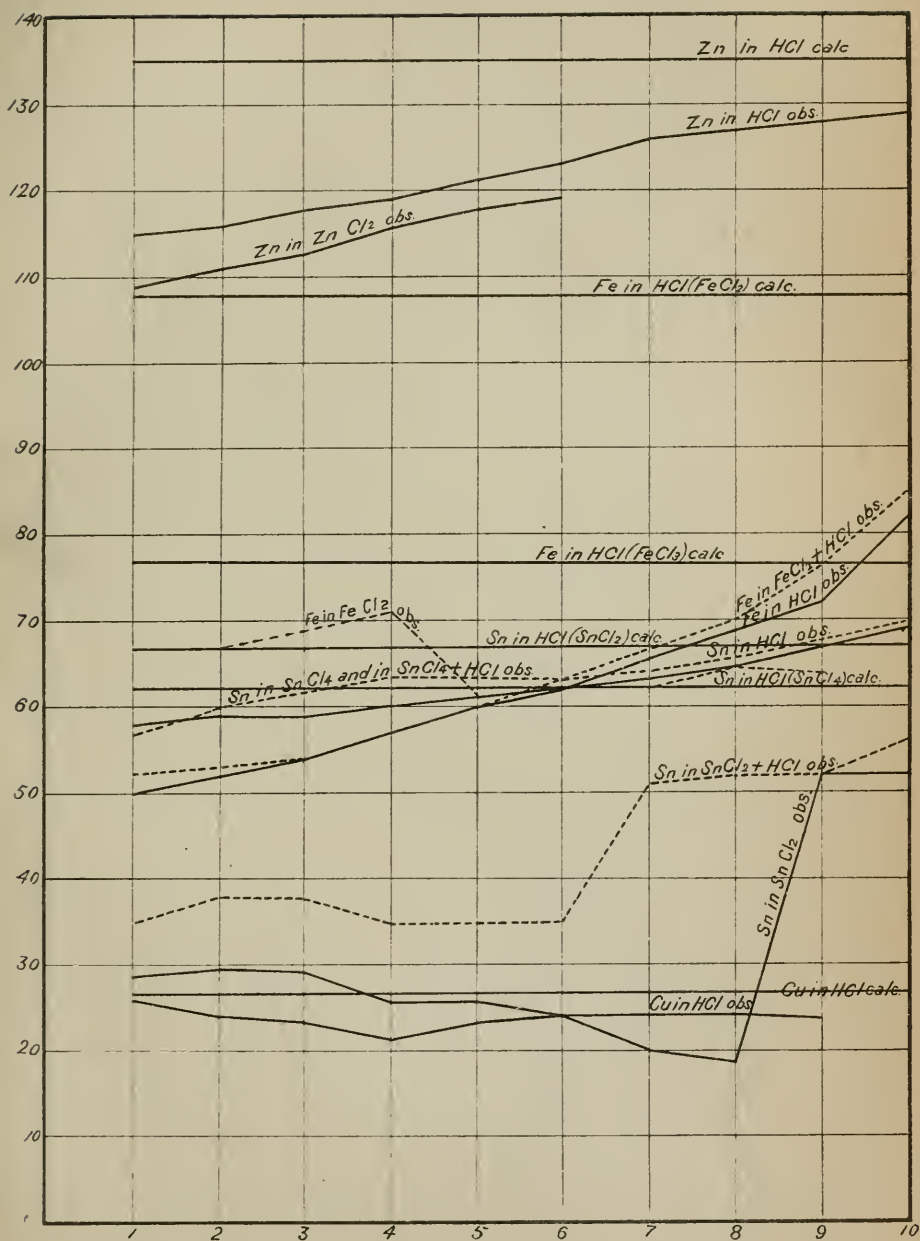
Wherefore for zinc the electromotive force should be

$$EF = 0.00004302 \cdot (17120 + 14350) \text{ cals.} = 1.35 \text{ V.}$$

Similarly, for copper = 0.27  $V$ , for ferric iron = 0.76  $V$ , for ferrous iron = 1.08  $V$ , for stannic tin = 0.62  $V$ , and for stannous tin = 0.67  $V$ . These results are plotted in the accompanying Diagram No. 1 as straight lines.

The curved lines represent the observed electromotive force in hydrochloric acid and in solutions of the corresponding chlorides.

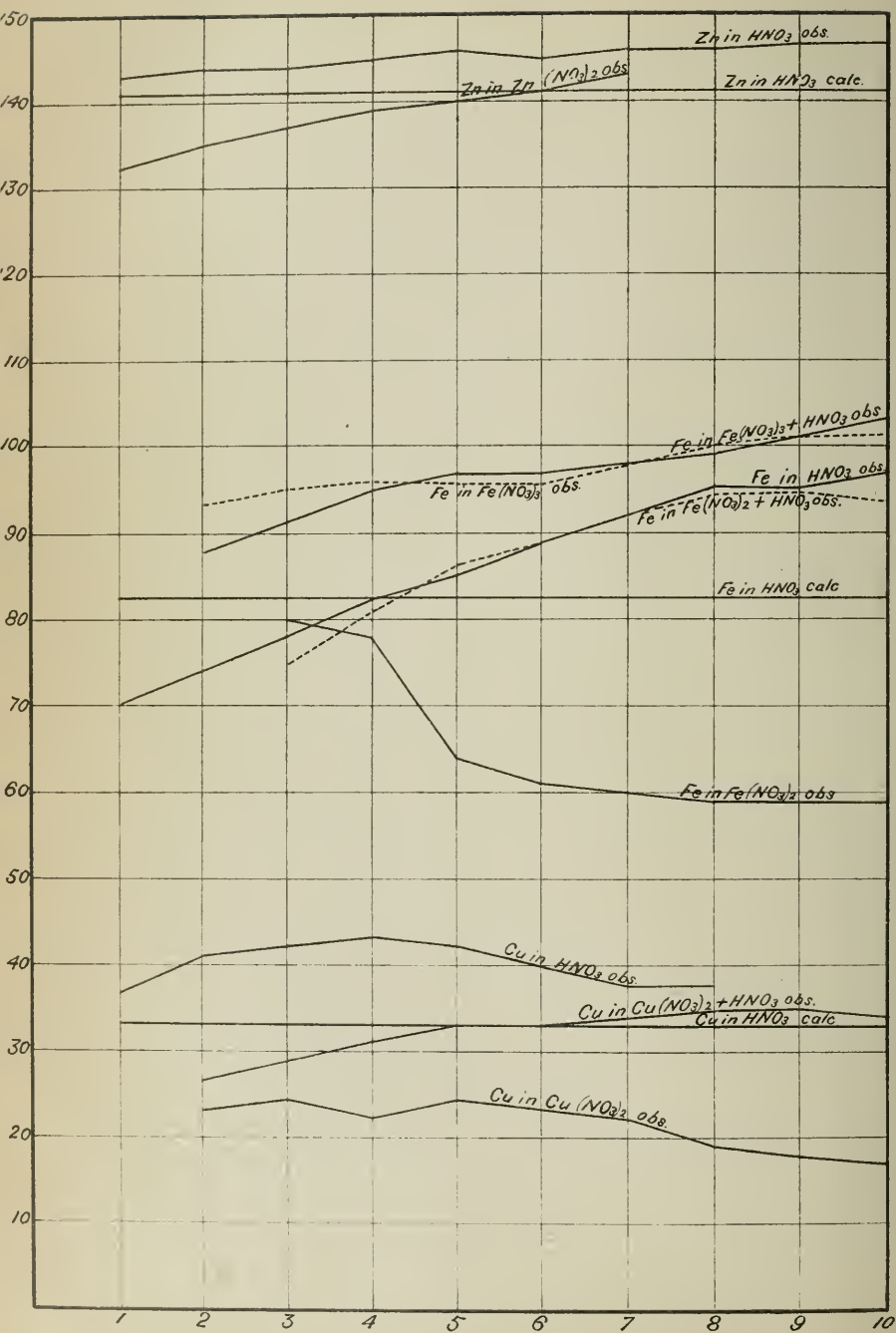
<sup>1</sup> Thermochemische Untersuchungen.











Results are also given for the nitrates in No. 2, where



Accordingly the calculated electromotive force should for zinc = 1.41 V, for copper = 0.33 V, and for iron = 0.82 V.

The curves show that although there is a general analogy between electromotive force and chemical energy, the two are by no means equal.

Particularly interesting is the difference in electromotive force between the *-ous* and *-ic* compounds. The heats of formation of *-ous* salts are probably greater, for equivalent quantities, than those of *-ic* compounds, and consequently, the calculated electromotive forces also should be higher. Yet the observed values of the *-ous* salts are lower. True, it may be urged that a minute quantity of an *-ic* salt is formed and consequently the value depreciated, as this is in general controlled by the lower electromotive force. But the conditions are all unfavorable to the formation of these compounds, and with iron and tin, only *-ous* chlorides are obtained by the processes supposed to take place in the cells. Can we find an explanation in the dissociation hypothesis and the one above?

As non-conductors have negative electricity so interwoven in their texture that very little, if any, motion of electricity can take place within the atom, when such an atom approaches and touches a mass of metal the negative ion will attract a quantity of the positive ion containing a unit charge and go off with it as a chemical compound. This, as containing the largest quantity of metal, will be the *-ous* compound. Before migrating far it will meet negative ions, and possessing a comparatively large charge of positive electricity, may give up a part, but never without accompanying matter, to the second negative ion, thus forming a compound relatively richer in negative ion or an *-ic* compound. The quantity of electricity in the positive ion of this being so much less than in the positive ion of an *-ous* salt, when a quantity of an *-ic* salt is formed equivalent to one atom of the negative ion the heat evolved is necessarily much less than that yielded in the formation of a corresponding quantity of an *-ous* salt.

Again, in the preceding explanation of electromotive force a

dynamical equilibrium was supposed—an equilibrium resulting from a charge of the electrode with negative electricity by the negative ion and a partial removal of that electricity by the positive ion. As the charge of the positive ion is much smaller in the *-ic* condition, the electricity removed is also much less, and the potential is therefore higher. Of course the action is similar on both electrodes, but the electrode least affected in the first case is presumably least affected in the second, and the result is an increased difference of potential or rise of electromotive force.

In this or some similar way it seems that an explanation is to be found; whether it will suffice for all cases future experiments alone can decide. A change of internal energy in the way of dissociation must not be overlooked, but it is hard to think that this can account for such a difference of electromotive force as is observed in solutions of *-ous* and *-ic* salts.

It would therefore be of great interest to extend determinations to all metallic salts, more especially to metals forming *-ous*, *-ic* and *per-* salts, and to determine if there are any solutions in which dilution lowers the electromotive force while secondary action is excluded. But other work, in the meantime begun, will demand attention, so that these results are now published in the hope that some one will feel inclined to carry the matter farther.

UNIVERSITY OF MISSOURI, *June*, 1891.

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## NOTES ON DIAZOBENZENE PERBROMIDE.<sup>1</sup>

BY CHARLES E. SAUNDERS.

This work was undertaken for the purpose of studying the conduct of diazobenzene perbromide and of triazobenzene (diazobenzene-imide of Griess) towards various reagents, and especially the products obtained by treating the former substance with substituted ammonias, as it appeared highly probable that the work of Griess<sup>2</sup> in this direction had not been correctly interpreted by him. Shortly, however, after the commencement of the investi-

<sup>1</sup> The author wishes to express his sincere thanks to Professor Remsen for his kindness in directing the work of which an account is here given.

<sup>2</sup> Phil. Trans. 1864, 673.



gation an article<sup>1</sup> was published in one of the journals, from which it appeared that somewhat similar work was being carried on elsewhere, so that it seemed best not to continue the research in the direction originally intended. Nevertheless a few observations which may be worthy of notice were made.

*Preparation of Diazobenzene Perbromide.*

The most convenient method found was to prepare diazobenzene sulphate according to the method of Knoevenagel,<sup>2</sup> dissolve in a little water, filter quickly, and then add with constant stirring an excess of a cold solution of bromine in moderately concentrated hydrobromic acid. The perbromide separates under these circumstances as a dark-colored, pasty mass which can easily be removed from the aqueous solution of the acid. By washing with several portions of pure ether the perbromide is partly purified and is obtained as a reddish-brown solid with a strong bromine-like odor. By exposing this solid, spread out on drying-paper, to the air for about an hour the odor disappears almost entirely and the color of the substance fades to a yellowish-brown. It is then in a condition fit for use. When prepared according to the method of Griess—using a solution of bromine in quite dilute hydrobromic acid—the crude product is precipitated as a dark liquid much like bromine. This seems to have been regarded by Griess as a comparatively pure product. It appears probable, however, that this liquid condition is due to the presence of more bromine than is required by the formula  $C_6H_5N_2Br_3$ . In support of this may be mentioned the fact, observed by Griess, that the perbromide can be obtained in solid condition by treating the liquid product with ether. That author does not explain this action of ether, but it seems to be most easily understood by supposing that the solvent removes the excess of bromine from the liquid and thus allows the perbromide to separate in its natural condition. It may be, however, that the ether dissolves out some definite chemical compounds formed between bromine and diazobenzene perbromide, and which, while present, keep the remainder of the perbromide in a liquid state. The ether used for washing the liquid or pasty perbromide always becomes highly colored as if by bromine.

<sup>1</sup> Gaz. Chim. It. **20**, 798.

<sup>2</sup> Ber. d. chem. Ges. **23**, 2994.

In the present investigation a further fact was discovered bearing on this point. When pure, dry diazobenzene perbromide is subjected to the action of bromine vapor, mixed with air, at ordinary temperatures it takes up bromine and is rapidly converted into a liquid. If the action be not allowed to go very far the perbromide can be recovered, in part, in solid condition by treatment with ether. Quantitative experiments were made for the purpose of determining whether by the action of bromine vapor a liquid compound of definite composition could be obtained. This was not found possible. The proportion of bromine taken up varies with the amount of air mixed with the vapor. In one experiment where air was almost entirely absent the perbromide took up several times its weight of bromine in twenty-four hours. The method of treatment in this case was to place a beaker containing the solid perbromide beside a beaker containing bromine. The two were then covered with a bell-jar which was almost air-tight. Under these circumstances 1.0655 grams of solid perbromide took up 3.9493 grams of bromine.

While these experiments failed to prove the formation of any single, definite compound, there seems to be no doubt that bromine enters into combination with diazobenzene perbromide. It appears, therefore, highly desirable that in all experiments with this substance it should be first of all purified by washing with ether and obtained in dry condition. Symmetrical tribrombenzene was the only other impurity recognised in the perbromide as obtained in pasty condition by the method described. It was identified by a careful comparison with the product obtained from tribromaniline. Washing the perbromide by rubbing it up in a mortar containing ether will remove the tribrombenzene, but not without difficulty.

#### *Decompositions of Diazobenzene Perbromide.*

On being allowed to stand in bromine water, it forms tribromphenol. Hence a considerable amount of this product is formed by allowing the contents of the beaker in which the perbromide has been made to stand over night. The reaction takes place quickly if the solution is heated.

When diazobenzene perbromide is boiled with pure water the chief products formed are tribromphenol, phenol, hydrobromic acid, free nitrogen and free bromine. The tribromphenol was

identified by comparison with the substance as obtained directly from phenol by the action of bromine water.

The presence of phenol was proved by the color-reactions of, and the action of bromine water on, the distillate obtained by passing steam through the original liquid.

According to Griess, when diazobenzene perbromide is warmed with alcohol there is formed, almost quantitatively, monobrombenzene. This observation appears to be incorrect. By heating the perbromide with absolute alcohol to boiling, adding water, and then distilling with water-vapor, a heavy oil was obtained, which was dried by calcium chloride and then subjected to fractional distillation. It was easily separated into two principal portions, one of which boiled at  $155^{\circ}$ – $157^{\circ}$  and was evidently monobrombenzene, while the other boiled considerably above  $200^{\circ}$ . After several distillations, that fraction of the high-boiling product was taken which passed over between  $228^{\circ}$  and  $233^{\circ}$  (uncorr.). The percentage in this was then determined by the method of Carius, the heating being carried on for fourteen hours at about  $170^{\circ}$ . 0.2930 gram substance gave 0.2790 gram AgBr, which represents 40.52 per cent. of bromine, the amount required by the formula  $C_6H_4BrOC_2H_5$  being 39.80 per cent. Lippmann<sup>1</sup> obtained monobromphenetol by the action of bromine on phenetol and also by the action of the potassium salt of (para)bromphenol on ethyl iodide. He gives the boiling-point of the product as  $233^{\circ}$ . It is evident, therefore, that the substance obtained in this case was parabromphenetol, identical with that of Lippmann, though the analysis and the variation in boiling-point show that it was not pure. The bromphenetol was found very difficult to solidify. It was solidified, however, by the action of solid carbon dioxide and ether. Its melting-point proved to be  $+4^{\circ}$ . This had not been previously determined.

The decomposition of the perbromide by hot alcohol was performed a number of times, and bromphenetol was always found to be produced in considerable quantity. Brombenzene formed, as a rule, less than one-half of the total liquid products by volume. It appears, therefore, that when hot alcohol acts on diazobenzene perbromide, the chief products of the reaction are parabromphenetol and monobrombenzene. Hydrobromic acid and free nitrogen are of course formed, as well as several other substances

<sup>1</sup> Wien. Akad. Ber. (2 Abth.) 62, 611.

both solid and liquid. The formation of a phenetol derivative in this case accords with the observation of Remsen and Orndorff,<sup>1</sup> that diazobenzene nitrate when heated with alcohol gives a very large proportion of phenetol, and not simply benzene as first stated by Griess. Many other examples of the formation of ethoxy compounds under similar circumstances might be cited.

When the perbromide is kept for several hours in boiling ether, brombenzene is formed in considerable quantity. With glacial acetic acid it is also formed, though in smaller proportion, and associated with another liquid (possibly a brom-phenyl acetate) of much higher boiling-point. On standing in a desiccator over caustic potash the perbromide gradually decomposes with loss of color. The products formed were not investigated. In general terms it may be said that diazobenzene perbromide has a decided tendency to yield monobrombenzene as one of its decomposition products, but that almost all of the reactions in which it is involved result in the formation of too many products to render the substance very useful in chemical investigations.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY.

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## REVIEWS AND REPORTS.

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### RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.

#### V.—*Ammonia, Nitric Acid, Explosives.*

##### *Ammonia.*

*Sources.*—Practically all the ammonia of commerce, which in the form of sulphate finds extensive use as a fertilizer, is still obtained from the nitrogen of coal. Nearly the whole of that obtained from this source is prepared from the ammoniacal liquor of the gas-works, and but little progress has been made in the direction of regaining the immense quantities of ammonia given off in the combustion of coal as fuel.

Most varieties of coal contain 1.3–1.5 per cent. of nitrogen.

<sup>1</sup> This Journal 9, 387.

According to Lunge,<sup>1</sup> assuming the total quantity of coal burned to be 400 million tons, this would be equivalent, if all the nitrogen could be obtained as ammonia, to 26 million tons of ammonium sulphate, or about 200 times the total amount actually obtained. More than 90 per cent. of this coal is, however, burned as fuel under conditions which make the recovery of the nitrogen as ammonia very difficult. From the portion used in gas-making, also, only about one-seventh of the nitrogen contained in the coal is practically obtained in the form of ammonia, the remainder chiefly remaining in the coke or passing off as free nitrogen.

Smaller quantities of ammonia are also obtained from the gases given off from coke-ovens and blast-furnaces, and in the distillation of shale. The following table, taken from the reports of the English Alkali-Inspector, gives the relative amounts of ammonium sulphate obtained in Great Britain from these various sources within the past four years:

	1886. Tons.	1887. Tons.	1888. Tons.	1889. Tons.
Gas works . . . . .	82,500	85,000	93,000	100,000
Iron works . . . . .	4,000	5,000	5,300	6,000
Shale distilling works . . .	18,000	21,000	22,000	23,000
Coke and carbonising works,	2,000	2,700	2,500	3,000

While it appears practically out of the question to save the ammonia yielded when coal is burned directly for heating purposes, there are two methods of using coal as fuel in connection with which immensely increased quantities of ammonia might easily be obtained; these are the manufacture of coke in coke-ovens, and the production of gaseous fuel. From these sources we may expect to see in the future the great increase in the world's production of ammonia.

The amount of coal converted into coke, chiefly for metallurgical purposes, is not far from 10 per cent. of the total coal produced. If we assume that the amount so treated is 40 million tons, and that 20 lbs. of ammonium sulphate are obtained from one ton of coal, we find that if all the ammonia given off in the coking of coal were regained, not less than 400,000 tons of ammonium sulphate would be obtained from this source. Nearly all the coke produced is, however, made in *bee-hive* or similar ovens, in which the gaseous products and a portion of the coal are burned in order to carbonise the remainder; with these ovens the saving of the ammonia is impracticable. Flue-ovens, in which the coal is coked in closed chambers by the heat of the burning gas circulating through flues in the side walls, like those on the *Coppée* or *Simon-Carvès* system, have been introduced to some extent in Europe, and their use is gradually extending. These permit the recovery of the ammonia and tar given off; the chief

<sup>1</sup> Thorpe's Dict. "Ammonia."



obstacle to their adoption has, however, been their high first cost. In this country several attempts have been made to use this form of oven and recover the by-products, but these attempts have always been abandoned. Certain forms of flue-oven have been greatly cheapened and simplified during the past few years, and have proved very successful and economical in Germany, so that the introduction of this improved process in this country, with production of ammonia as a by-product, is probably only a question of time.

The possibility of obtaining ammonia as a profitable by-product in the conversion of coal into fuel-gas in gas-producers has lately been demonstrated by the experiments of Mond.<sup>1</sup> It was found that a good yield of ammonia could only be obtained by keeping the temperature in the producers very low, and by the use of an amount of steam equal to about twice the weight of the coal consumed. Under these circumstances about half the nitrogen is obtained in the form of ammonia, giving a yield of 70 pounds of sulphate per ton, or more than three times the yield commonly obtained in the gas-works. Mond's process, which is in operation on a large scale at the soda-ash works at Norwich, England, is fully described in the paper to which reference is given. Very complicated apparatus is required for the cooling of the large volume of gas produced, the condensation of the steam, and the absorption of the ammonia by acidified ammonium sulphate solution. The fuel-gas obtained contains, by percentage, 15 of carbon dioxide, 10 of carbon monoxide, 23 of hydrogen, 3 of hydrocarbons, and 49 of nitrogen. It is therefore of somewhat lower heating power than ordinary producer-gas. According to Mond, its calorific power is equal to 73 per cent. of that of the coal from which it is made. The actual cost of the ammonium sulphate produced, including fuel consumed, labor, etc., is about £5 per ton, or less than half the present price in England. The cost of the plant is very considerable, and it is stated that the process can be successfully worked only by large consumers of cheap fuel. Mr. Mond remarks that if only one-tenth of the fuel consumed in England were treated by this process, that country could supply an amount of sulphate of ammonia equivalent to the whole quantity of that salt and of nitrate of soda used in the Old World for fertilising purposes.

*Fixation of Atmospheric Nitrogen.*—Attempts have long been made to bring the nitrogen of the air into combination with carbon or hydrogen and thus obtain cyanides or ammonia. The history of these experiments has lately been fully reviewed by Breneman<sup>2</sup> and by Fawsitt.<sup>3</sup> The only methods which have yielded any encouraging results consist in passing nitrogen over white-hot charcoal previously saturated with an alkali; a cyanide is thus produced

<sup>1</sup> J. Soc. Chem. Ind. (1889), 505.

<sup>2</sup> J. Amer. Chem. Soc. 11, 1-45.

<sup>3</sup> J. Soc. Chem. Ind. (1890), 30.

which, if ammonia is desired, may be subsequently decomposed by steam. The process of Possoz and Boisière was carried out in 1843 on a manufacturing scale by Bramwell & Hughes of Newcastle. Fire-clay retorts were filled with wood-charcoal previously impregnated with potassium carbonate; after raising the retorts to a white heat, air was passed through them for a certain time, the contents were then cooled, lixiviated, and the cyanide obtained converted into ferrocyanide by treatment with ferrous sulphate. In this way two tons per week of ferrocyanide were obtained from a bench of eight retorts. From a commercial point of view the process was a failure, owing to loss of potash and wear and tear of the plant; it was therefore abandoned in 1847. A similar process employed by Fawsitt, using sodium carbonate with a view to the production of ammonia, led to equally unsatisfactory pecuniary returns.

Mond<sup>1</sup> has recently made experiments on a manufacturing scale with the process of Marguerite and Sourdeval (Eng. pat. 1860), in which barium carbonate is the alkali employed. This was made into balls with charcoal and pitch; after calcining in a reducing flame the balls were charged into vertical fire-clay retorts heated to a temperature of 1400° C., and submitted to the action of a current of nitrogen obtained from the carbonating towers of the ammonia-soda process. After a certain time about 40 per cent. of the barium oxide present was converted into cyanide; the briquettes were then dropped into a closed cooling-chamber and finally treated with steam, by the action of which ammonia was formed and the carbonate regenerated. Owing to the difficulty of securing fire-clay retorts which would resist the high temperature employed, Mr. Mond was obliged to abandon the experiments; he is, however, of the opinion that the difficulties can be overcome, and that the process will prove remunerative for the manufacture of cyanides.

### *Nitrates.*

Until twenty years ago nearly all the saltpetre, or potassium nitrate, of commerce was obtained from India, where it is collected in the form of an incrustation upon the soil in thickly populated regions, arising from the gradual oxidation of animal organic matter. The supply of saltpetre from this source has decreased, and now amounts to about 25,000 tons per year. A large quantity of saltpetre was also made in this country, in the early part of this century, by leaching the earthy matter dug up in caves, chiefly in the Mammoth Cave, Ky.

The deposits of sodium nitrate, or Chili saltpetre, near the sea-coast of Chili, in the province of Tarapaca and the desert of

<sup>1</sup> Loc. cit.

Atacama, have lately been fully described in a most interesting report by Consul Walker, of Bogota.<sup>1</sup> These deposits have been known and worked for nearly seventy years. They extend a distance of 260 miles along the coast, and have in some places a depth of over six feet. The total amount of available material has been estimated to be 178 million tons. The presence of 20 per cent. of salt and 0.05 per cent. of iodine in the mineral indicates that it has been formed by the gradual oxidation of the nitrogenous matter of seaweed. The "caliche" is refined by recrystallisation from water, and comes into commerce 95-98 per cent. pure. The exportation of nitrate of soda from Chili amounted in 1888 to 785,000 tons (of 1000 kilos), and in 1889 to 921,000 tons. By far the larger part of this product is used in agriculture.

Potassium nitrate is now chiefly obtained by treating the Chili nitrate of soda with potassium chloride from Stassfurt. More than 50,000 tons of the nitrate of soda produced in 1888 was used for this purpose, and Pfeiffer<sup>2</sup> states that 41.2 per cent. of the potassium chloride produced at Stassfurt is employed in this industry. The production of potassium chloride in 1888 was 123,550 tons; 41.2 per cent. of this is 51,000 tons, which would correspond to an annual production of nearly 70,000 tons of artificial saltpetre.

### *Explosives.*

The most recent advances in the manufacture of explosive materials have lately been summed up in an interesting manner in papers by Abel<sup>3</sup> and McRoberts.<sup>4</sup>

All explosive compounds hitherto used for fire-arms and ordnance have possessed two defects, viz. too rapid combustion, and the evolution of dense volumes of smoke. The efforts of inventors during the past decade have largely been expended in the direction of overcoming these drawbacks.

Gunpowder, which burns with moderate rapidity, produces more smoke than other explosives. Nearly 50 per cent. of the products of combustion of gunpowder are non-gaseous, and the white smoke produced consists chiefly of potassium carbonate, sulphate and sulphide, in a state of fine division. This large proportion of solid products adds greatly to the corrosion of the bore of the gun. Nobel's experiments have shown that those substances which on explosion liberate the largest proportion of gas and develop the least heat produce the least corrosive effect.

The rapidity of combustion of gunpowder may be to a considerable extent decreased by moulding into larger grains and submitting these to heavy pressure, as is commonly the practice in the manufacture of powder for heavy guns. A further advance

<sup>1</sup> U. S. Consular Reports, No. 114, March, 1890.

<sup>3</sup> Royal Institution Lecture, Jan. 31, 1890.

<sup>2</sup> Chem. Industrie (1888), 129.

<sup>4</sup> J. Soc. Chem. Ind. (1890), 476.

in this direction is the introduction of the brown "cocoa-powder," which has lately come into extensive use in Germany. This contains much more saltpetre and less sulphur than ordinary gunpowder; the charcoal it contains is also but slightly burned, and gives the powder a brown shade. This explosive burns more slowly than ordinary powder, and thus produces a gradual and sustained effect upon the projectile. It is said that the smoke produced disappears with extraordinary rapidity, probably owing to the solution of the solid products in the relatively large proportion of water produced, in the form of vapor, on explosion.

Gun-cotton and nitro-glycerine produce little or no smoke when fired. Owing to the difficulty of controlling or retarding the sudden combustion of these substances, however, they have never been successfully adapted for use in fire-arms, in spite of the large amount of patient experiment which has been expended upon this problem.

The first nearly smokeless powder was probably that introduced by Colonel Schulze, of the Prussian Artillery. This consisted of small particles of wood, purified, partially converted into nitro-cellulose, and mixed with potassium chlorate. Within a few years much interest has been aroused by the report that the French government had secured the secret of a perfect smokeless explosive, called the "*Vieille powder*," or *poudre B*. It is now known that this was a compound of picric acid; it has been supplanted by later discoveries.

The invention of *blasting gelatine*, by Nobel, in 1875, opened the way to the successful application of such powerful explosives as nitro-glycerine and gun-cotton to military purposes. Nitro-glycerine, as is well known, contains an excess of oxygen over that required to completely burn the carbon and hydrogen contained in it, while gun-cotton shows a slight deficiency. *Blasting gelatine* is a translucent, elastic substance, made by dissolving about eight parts of nitro-cotton in ninety-two parts of nitro-glycerine. The nitro-cotton is a lower degree of nitration of cellulose, similar to collodion cotton. This new explosive is unaffected by water, does not readily explode by percussion, and when detonated explodes with an energy greater than that of either of its constituents. By suitable additions of inert material the rapidity of its explosion may be moderated, and its usefulness for blasting purposes thus greatly increased. This may also be effected by increasing the proportion of nitro-cotton, and in this way a mixture suitable for the ordinary uses of gunpowder may be obtained. The most successful modern "smokeless powders" are of this character.

Nobel's smokeless powder, "*balistite*," consists of about equal parts of nitro-glycerine and soluble nitro-cotton, with the addition of a small proportion of camphor for the purpose of bringing about the combination of the materials; the effect of the camphor



is also to greatly moderate the violence of the explosion. Another smokeless powder, "cordite," invented by Abel and Dewar, is a similar mixture of nitro-glycerine and ordinary gun-cotton, the combination of the two being brought about by the aid of acetone or other solvents; camphor or tannin is added to reduce the rapidity of the explosive action. These powders are similar to blasting gelatine in appearance, and are used in the form of small cubical grains. They are even more gradual in their action than gunpowder, and the rapidity of explosion can be modified to any desired degree by the addition of suitable proportions of camphor, etc. These powders are almost absolutely smokeless, and seem to be capable of successful use in small-arms or cannon. Experiments are now being carried on by several governments with a view to testing the efficiency of the new explosives, and determining the methods by which they can be most safely stored, transported and handled.

SPENCER B. NEWBURY.

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#### STEREOCHEMISTRY.<sup>1</sup>

##### I.—*The Stereochemistry of Carbon.*

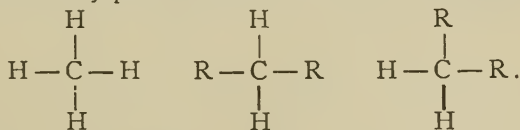
It is only seventeen years since the theory of geometrical isomerism first took definite form. Yet the study of structural isomerism dates from 1824, and in 1830 the comparison of tartaric with racemic acid brought even Berzelius to admit that substances of like composition could have unlike chemical properties, and caused him to propose the term isomerism for such cases. The conception of isomerism was that of compounds containing the same elements in the same proportions and yet differing in properties; the difference being due to the different grouping of the elements in the different compounds. The conception of geometrical isomerism is that of compounds containing the same elements in the same proportions and arranged in the same groups, and yet differing in properties; the difference being due to the different arrangement in space of the constituent groups of the several compounds. The second conception is thus a natural outgrowth of the first. The growth seems not great; the time required for it—more than forty years—seems at first sight disproportionately long. But in this time much had to be done. The first conception has for its basis a knowledge of composition, quantitative as regards the elements present. Identity of composition proven, difference of grouping was inferred; and under the stimulus of the radicle-theory and its successors the work of testing compounds, among others isomeric compounds, for the presence or absence of certain groups went on rapidly. But this qualitative detection of groups was not enough: the second conception has

<sup>1</sup> Based on lectures delivered at Cornell University.



for its basis a knowledge of composition, quantitative as regards the groups present. To prove the structural identity of two molecules it was not enough to show that every group which had been found in one might also be detected in the other; it had to be shown that the whole structure of each molecule was expressed by its division into these groups; that no difference in sub-grouping due to structural isomerism within the primary groups was possible. Thus only in 1873 was it possible for Wislicenus, by demonstrating that the groups  $\text{CH}_3$ ,  $\text{OH}$ ,  $\text{CH}$ , and  $\text{COOH}$  were present in sarcolactic, as well as in ordinary lactic acid, to prove the structural identity of these acids. On this proof was based the dictum of Wislicenus: "The facts compel us to explain the difference between isomeric molecules having the same structural formulæ by the different arrangement of their atoms in space." "Words," says Van't Hoff,<sup>1</sup> "which I wish to quote because they set me thinking" ("ils m'ont mis à réfléchir sur le problème en question"). It was, then, a comparison of the number of isomers derivable from an ordinary structural formula with the number derivable from a formula representing "the arrangement of the atoms in space" that led Van't Hoff to the conception of his theory.

For the ordinary formulæ represent the atoms as if they all occupied the same plane. Now the number of isomers  $\text{CH}_2\text{R}_2$  derivable from any plane-formula for  $\text{CH}_4$  is two or more:



The only arrangement which excludes the possibility of isomerism is an arrangement in which all the hydrogen-atoms are equidistant from one another as well as from the carbon-atom; an arrangement possible only in three dimensions (Fig. 1).

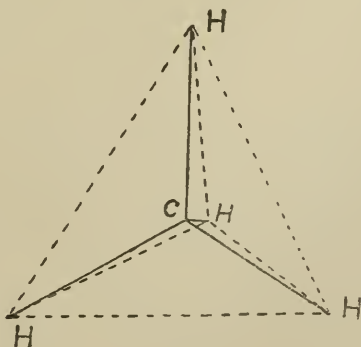


FIG. 1.

<sup>1</sup> "Dix années dans l'histoire d'une théorie" (Rotterdam, 1887), p. 24.

Thus the single fact that only one  $\text{CH}_2\text{R}_2$  can exist compels us to adopt for  $\text{CH}_4$  a three-dimensional formula—to suppose that the hydrogen-atoms are arranged round the carbon-atom as the corners of a regular tetrahedron round the center of it.<sup>1</sup> This conception had already been embodied in the carbon-model of Kekulé.

*The Theories of Van't Hoff and of Le Bel.*

But Van't Hoff went farther and, noting that this formula admits of isomerism only in one case, viz. when a different radicle occupies each corner of the tetrahedron, he recognised the peculiarity of this isomerism:

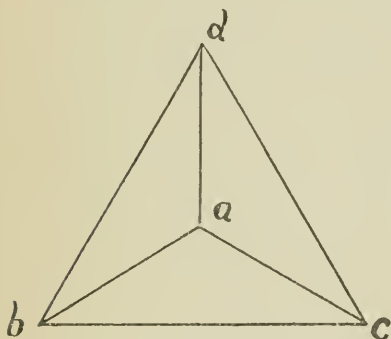


FIG. 2.

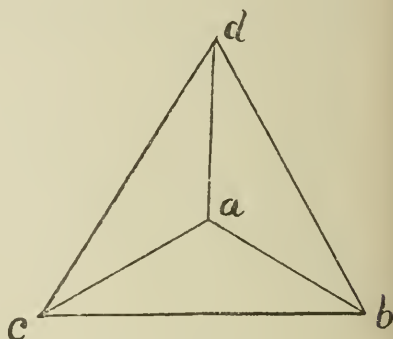


FIG. 3.

that it depends only on the order in which the groups are arranged, and that the isomers bear to one another the relation of object and image (Figs. 2 and 3).<sup>2</sup> On account of the lack of symmetry imparted to a regular tetrahedron by making every corner of it different, Van't Hoff called a carbon-atom combined with four different radicles an asymmetric carbon-atom (henceforth written C).

For proof that the peculiar isomerism demanded by his formulæ

<sup>1</sup> Such was the reasoning relied on by Van't Hoff and universally accepted as sound until last year, when Le Bel published a remarkable paper on "The conditions of equilibrium of the saturated compounds of carbon" (Bull. Soc. Chim. [3] 3, 788). The assumption underlying the argument just given is that when  $\text{CH}_3\text{R}$  is formed from  $\text{CH}_4$ , R takes the place of one of the H atoms; an unwarranted assumption, says Le Bel, for the position (or positions) of equilibrium of the system  $\text{CH}_3\text{R}$  depends on the particular properties of the elements of which this system is composed, and not on the position which the elements may have occupied in the system  $\text{CH}_4$ . That each of these systems has only one position of equilibrium tells us nothing as to the configuration of either; the hydrogen atoms of  $\text{CH}_4$  may be quite irregularly disposed, and yet the number of compounds  $\text{CH}_3\text{R}$  may not exceed one. Le Bel points out, however, as Wislicenus did, in the second edition of his treatise (p. 78), that the crystal-forms of most substances of the type  $\text{CR}_4$  indicate that their molecules have the symmetry of the regular system. So that the symmetrical tetrahedral configuration of these substances is a result of observation, though, as has been shown, not a theoretical necessity.

<sup>2</sup> It is only for convenience that Van't Hoff represents  $\text{C}abcd$  by a regular tetrahedron—a figure which really represents only such compounds as  $\text{C}_4$ , for difference among the radicles involves inequality of the forces connecting them with carbon and with one another; hence the distances  $\text{Ca}$ ,  $\text{Cb}$ ,  $\text{Cc}$ ,  $\text{Cd}$  are all different, and  $\text{C}abcd$  is properly represented by a tetrahedron quite irregular. This is important when we have to consider the interaction of radicles attached to two linked tetrahedra.

really existed, Van't Hoff pointed to the right-handed and left-handed modifications of substances which rotate the plane of polarised light; to the fact that this property of rotation is in the case of solutions peculiar to substances which contain *C*, and to the fact that the relation between his formulæ for the two modifications—the object-and-image relation—is identical with the relation between the crystal-forms of the two modifications.

Van't Hoff published his theory in Dutch in September, 1874;<sup>1</sup> Le Bel's paper on the same subject appeared in November, 1874.<sup>2</sup> A number of cases of unexplained isomerism had led Van't Hoff to his theory of optical activity. With Le Bel the attempt to account for optical activity led to the suggestion of three-dimensional formulæ, and so to a consideration of the number of isomers deducible from such formulæ. Not the chemical researches of Wislicenus, but the physical phenomena observed by Pasteur, Rammelsberg and Reusch, and accounted for theoretically by the mathematics of Sarrau, formed his starting point. For these established the coincidence of rotatory power in *solids* with a certain characteristic arrangement of their *particles*—an arrangement characteristic in its lack of symmetry—the lack of symmetry being complementary in the case of the two forms of a substance which rotate to the right and to the left respectively, so that while it suffices to prevent superposition of the two forms, it leaves each the mirrored image of the other. And Le Bel supposed that in the case of substances which are optically active when *in solution*, this complementary asymmetry must exist in the arrangement of the *atoms* in the molecule. The usual statement (Victor Meyer,<sup>3</sup> v. Richter,<sup>4</sup> Pattison Muir,<sup>5</sup>) of Le Bel's theory is that he, as well as Van't Hoff, maintained that every substance optically active in solution contains *C*. What Le Bel<sup>6</sup> maintained was that "in general if a substance is derived from our primitive type  $MA_4$  by the substitution of three different atoms or radicles for  $A_3$ , its molecule will be asymmetrical and will possess the power of rotation." "Thus, if in the formula of a substance we find carbon combined with three monatomic radicles differing from one another and from hydrogen, the substance should be active" (p. 339). This is the converse of the usual statement. Further, since "*M* is a radicle simple or complex" (p. 338), it is *not* necessarily a single carbon-atom to which the four unlike groups must be attached to cause rotation. This is the reverse of the usual statement. The importance of reversing it is not merely historical, as will be seen later.<sup>7</sup> Le Bel, then, gave the case of a tri-substituted methane as only one example of the application of a principle. Ethylene derivatives might or might not prove to be optically active accord-

<sup>1</sup> "Dix années," etc., p. 13.

<sup>2</sup> Yet Pattison Muir, in his "Principles of Chemistry," ascribes the Van't Hoff-Le Bel theory to "Van't Hoff following Le Bel in 1875" (p. 181), to "Van't Hoff following in the steps of Le Bel" (p. 304, 2d ed.).

<sup>3</sup> Ber. d. chem. Ges. **23**, 574.

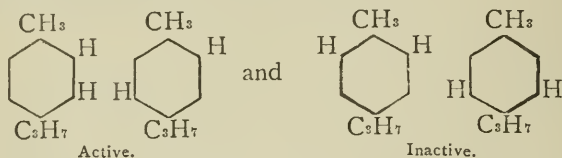
<sup>4</sup> Loc. cit., p. 304.

<sup>5</sup> Comp. Herrmann: Ber. d. chem. Ges. **21**, 1949.

<sup>6</sup> Organische Chemie, p. 47.

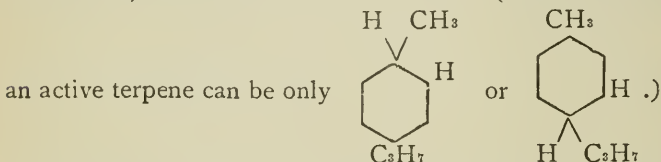
<sup>7</sup> Bull. Soc. Chim. **22**, 333.

ing as the hydrogen-atoms were or were not in the same plane. Tri-substitution products of benzene should be active. The asymmetry of the whole molecule, not the asymmetry of the groups attached to any one carbon-atom in it, was the criterion. Thus the formulæ of the terpenes would be



(This hypothesis was based on the assumption that the methyl and propyl groups do not occupy a plane of symmetry of the whole molecule, as would be the case if all the atoms of the terpenes were in the same plane as shown.)

Van't Hoff's theory, on the other hand, was that every substance active in solution—benzene-derivative or not—contains *C*. In every case in which the constitution of such a substance has been determined, this statement is borne out. (Thus the formula of



And Fock<sup>1</sup> has recently tried to show in detail the connection between *C* and the rotation of light. If of the radicles *a b c d* connected with *C*,  $a > b > c > d$ , then any rotation of these radicles will take place round the heaviest radicle *a* as axis, and more readily in the direction *bcd* than the other way. For *d*, the smallest radicle, is the thin end of the wedge (Fig. 4). Fock

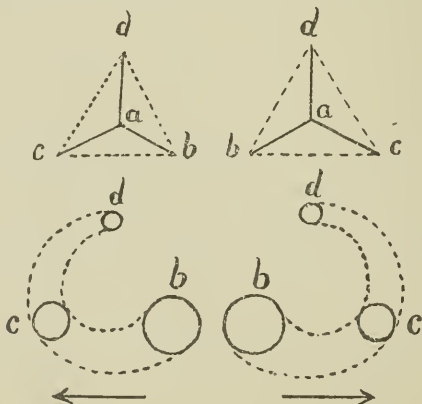
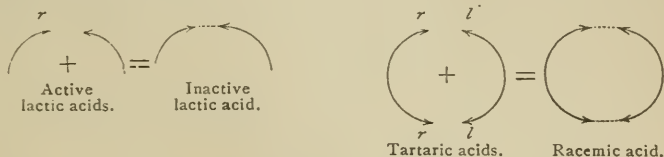


FIG. 4.

<sup>1</sup> Ber. d. chem. Ges. **24**, 101; compare Ostwald's criticism, Ztschr. phys. Chem. **7**, 429. See also the theory of Guye, Bull. Soc. Chim. [3] **3**, 595.

shows how such rotation would account for optical activity and for the way in which it is affected by solvents.

The converse of Van't Hoff's theory, the statement that every *C* group is optically active, has received confirmation in so many instances that it now has the support of Van't Hoff. This does not imply the belief that every *substance* containing *C* is optically active. A substance may contain molecules of equal and opposite activity in equal numbers, as in the case of racemic acid and of ordinary inactive lactic acid, the zinc salt of which has recently been made synthetically from the zinc salts of the right-handed and left-handed acids.<sup>1</sup>



Nor is the belief implied that every *molecule* containing *C* is optically active. The molecule may be divided against itself, possessing *C* groups of equal and opposite activity in equal

numbers, as is the case with mesotartaric acid, and probably

with erythrite,  $\begin{array}{c} \text{CH}_2\text{OH} \\ \text{CHOH} \\ \text{CHOH} \\ \text{CH}_2\text{OH} \end{array}$ , which yields mesotartaric acid on oxidation.

Substances containing only one *C* are, of course, excluded from this latter class, and all such substances should either be active or resolvable into two compounds of equal and opposite activity. "And in fact," says Van't Hoff,<sup>2</sup> "to this day no inactive substance of this class has resisted decomposition." "Fourteen times the 'doubling' has been attempted and the attempt has never been in vain."<sup>3</sup> But the usual methods of "doubling": the action of living organisms, which decompose one of the active isomers faster than the other; and the combination of the inactive with an active body, cannot always be applied. Easterfield<sup>4</sup> found this to be the case with chlor- and brom-phenyl-acetic acids, which proved to be inactive even when formed from active mandelic acid. Indeed, the only active substance containing a

halogen linked with *C* is amyl iodide,  $\begin{array}{c} \text{H} \\ | \\ \text{C}_2\text{H}_5 - \text{C} - \text{CH}_3 \\ | \\ \text{I} \end{array}$ . And

<sup>1</sup> Schardinger: Monats. für Chem. 11, 558.

<sup>3</sup> Loc. cit., p. 45.

<sup>2</sup> "Dix années," etc., p. 43.

<sup>4</sup> J. Chem. Soc. 59, 71 (1890).



of substances containing fewer than three carbon-atoms not one is known to be active though many contain C.<sup>1</sup>

Victor Meyer, in his interesting review of stereochemistry,<sup>2</sup> has proposed an explanation of this fact. Simple groups, it is said, are more mobile than complex ones; hence by changing places with one another they can bring about tautomerism. And mole-

cules of brom-nitro-ethane, *e. g.*  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}-\text{NO}_2 \\ / \quad \backslash \\ \text{H} \quad \text{Br} \end{array}$  in which the hy-

drogen-atom and, say, the nitro-group are constantly changing places, would have no more effect on polarised light than a mixture

of such molecules with  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}-\text{H} \\ / \quad \backslash \\ \text{NO}_2 \quad \text{Br} \end{array}$  in equal numbers.

For substances containing two C's, each combined with the same groups, two inactive forms are possible: one of the meso-

tartaric type  $\begin{array}{c} \curvearrowright \\ \curvearrowleft \end{array}$ , the other of the racemic type  $\begin{array}{c} \curvearrowright \quad \curvearrowleft \\ \curvearrowleft \quad \curvearrowright \end{array}$ ; but

only the former should be non-resolvable. Some substances, however, as dibrom-succinic acid<sup>3</sup> and hydrobenzoin, exist in two inactive forms, neither of which has yet been resolved. While

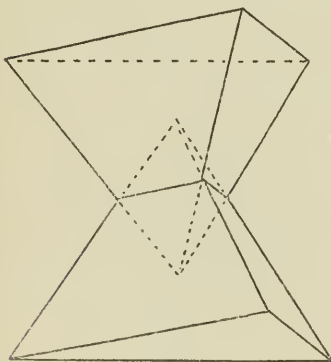


FIG. 5.

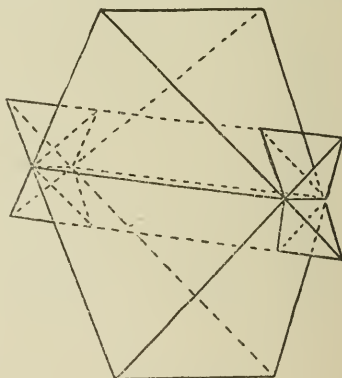


FIG. 6.

<sup>1</sup> Landolt: "Handbook of the Polariscopes." Translated by Robb and Veley (London, 1882), p. 29. Tables showing the relation between optical activity and composition are given.

<sup>2</sup> Ber. d. chem. Ges. 23, 567.

<sup>3</sup> Attempts at doubling derivatives of succinic acid which contain C are now in progress. Bischoff and Walden: Ber. d. chem. Ges. 23, 1957.

then the original statement of Van't Hoff that every substance active in solution contains *C* is proved without exception, the converse theory that every *C* shows optical activity except when this is neutralised by the activity of another *C*, requires further proof. Meanwhile no fact incompatible with it is known.

The extension of Van't Hoff's space-formulæ from a single carbon-atom to two combined carbon-atoms was simple. "The very fundamental principle of the tetrahedral arrangement demands that two carbon-atoms singly-linked shall occupy at once the center of one tetrahedron and the apex of the other."<sup>1</sup> (Fig. 5.) From this arrangement that for two doubly-linked carbons is deduced. (Fig. 6.)

It is now usual to represent singly-linked carbons by tetrahedra having an apex in common, the doubly-linked tetrahedra having an edge in common; this is simpler, and has so far sufficed to represent the facts.

In a substance of the formula  $CR^1R^2R^3R^4$  the distances separating the groups in the right-handed form are the same as in the left-handed form. Hence the resulting isomers are characterised by physical rather than by chemical differences. Another kind of isomerism results, however, from the arrangement of the *R*-groups in  $C_2R^1R^2R^3R^4$ . Here also two space-formulæ exist

for any one structural formula,  $\begin{array}{c} CR^1R^2 \\ || \\ CR^3R^4 \end{array}$ , viz. Fig. 7 and Fig. 8.

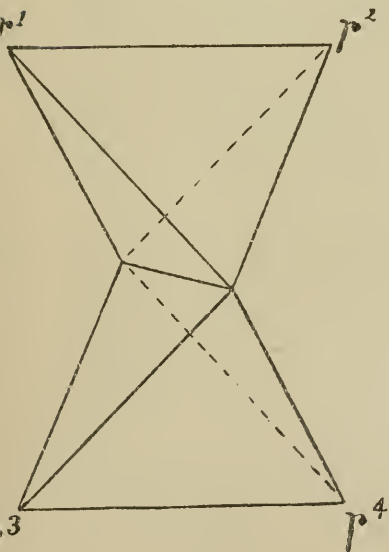


FIG. 7.

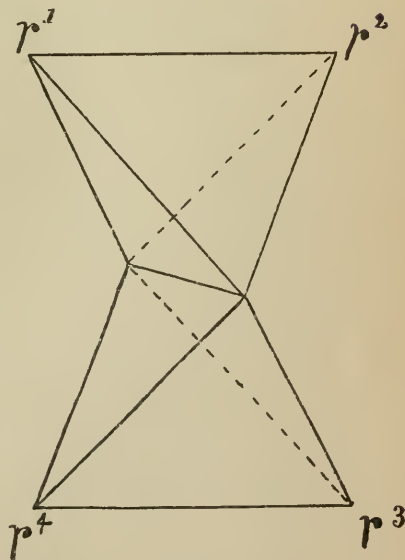


FIG. 8.

<sup>1</sup> Loc. cit., p. 52.

In Fig. 7  $R^1$  and  $R^3$  are nearer together than in Fig. 8; the same is true for  $R^2$  and  $R^4$ . Hence isomers of this type will be characterised by chemical differences. This isomerism will exist

also for substances of the type  $\begin{array}{c} \text{CR}^1\text{R}^2 \\ || \\ \text{CR}^1\text{R}^3 \end{array}$   $\left( = \begin{array}{c} \text{R}^1\text{CR}^2 \\ || \\ \text{R}^1\text{CR}^3 \end{array} \text{ and } \begin{array}{c} \text{R}^1\text{CR}^2 \\ || \\ \text{R}^3\text{CR}^1 \end{array} \right)$ ,

and of the type  $\begin{array}{c} \text{CR}^1\text{R}^2 \\ || \\ \text{CR}^1\text{R}^2 \end{array}$   $\left( = \begin{array}{c} \text{R}^1\text{CR}^2 \\ || \\ \text{R}^1\text{CR}^2 \end{array} \text{ and } \begin{array}{c} \text{R}^1\text{CR}^2 \\ || \\ \text{R}^2\text{CR}^1 \end{array} \right)$ , but not for  $\begin{array}{c} \text{C}(\text{R}^1)_2 \\ || \\ \text{CR}^2\text{R}^3 \end{array}$ ,

since  $\begin{array}{c} \text{R}^1\text{CR}^1 \\ || \\ \text{R}^2\text{CR}^3 \end{array} = \begin{array}{c} \text{R}^1\text{CR}^1 \\ || \\ \text{R}^3\text{CR}^2 \end{array}$ . To show that the number of isomers

foreseen by this theory is in accord with the facts we may cite the testimony of an opponent<sup>1</sup> of the theory, to the effect that substances possessing the same structural formulæ and containing two doubly-linked carbons united to different groups will exist in two isomeric forms. More than thirty such substances (besides derivatives), all presenting this isomerism, may be counted: among them are fumaric and maleïc acids, the crotonic and the cinnamic acids.<sup>2</sup>

ARNOLD EILOART.

(To be continued.)

SOLUTIONS. By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Being the fourth book of the second edition of Ostwald's "Lehrbuch der allgemeinen Chemie," with some additions. Translated from the German by M. M. PATTISON MUIR. Longmans, Green & Co.: London and New York, 1891.

A translation of even a portion of Ostwald's great "Lehrbuch" will be welcomed by all who use English with more ease than German. The work of translation, by Mr. Muir, is excellent. His style is clear and scholarly throughout. The accuracy of the translation is insured by the fact that Ostwald has revised the proofs of the English edition.

The object in offering this work to the public, as stated in the author's preface, is that "there are always objections to publishing a part of a book, but in the present case the issue of a part of a larger book seems to be justified by the consideration that a comprehensive survey of the very remarkable advances, both theoretical and practical, which have been made in the last few years in the subject of solutions must be useful to all who are not in a position to make themselves acquainted with the many and widely-scattered memoirs on this subject."

The most prominent characteristic of the entire "Lehrbuch der allgemeinen Chemie" is the importance attached to the physical side of chemistry. This feature is very pronounced in this

<sup>1</sup> Michael, Ber. d. chem. Ges. 20, 550.

<sup>2</sup> Liebermann, Ber. d. chem. Ges. 23, 2510, describes a third cinnamic acid not accounted for by the theory.

volume of 316 pages, which is almost entirely devoted to the discussion of the physical phenomena presented by solutions.

The book is divided into ten chapters. Chapter I. treats of solutions in gases. Chapter II.—Solutions of gases in liquids. Chapter III.—Solutions of liquids in liquids. Chapter IV.—Solutions of solids in liquids. Chapter V.—Osmose. Chapter VI.—Diffusion. Chapter VII.—Vapor-pressures of solutions. Chapter VIII.—Freezing-points of solutions. Chapter IX.—Salt-solutions. Chapter X.—Simultaneous action of several solvents.

This translation has appeared at an opportune moment. As is well known to readers of chemical literature, an active discussion has been carried on as to what takes place when one substance dissolves in another. The view that in solution the substance dissolved breaks down into simpler parts, the molecules themselves decomposing into their "ions," is held by such men as Van't Hoff, Arrhenius and Ostwald. A systematic treatise on this subject is furnished by this work on "solutions," and the book can be heartily recommended to all who are interested in one of the leading scientific discussions of to-day.

H. C. J.

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REPETITORIUM DER ORGANISCHEN CHEMIE. Von Adolf Pinner. Berlin, 1890.

Prof. Adolf Pinner has prepared a new edition of his excellent "Review of Organic Chemistry." Its popularity is shown by the fact that this is the ninth edition since 1872, and the popularity is deserved. The book is written for chemists beginning the study of chemistry, and for students of medicine and pharmacy. It differs for the better from most of its German rivals in two points. Under the title "methyl compounds," the halogen, hydroxyl, thio, nitrogen, and metal, substitution-products of methane are successively fully discussed, with constant reference to analogies with inorganic compounds; then the corresponding derivatives of ethane are taken up, followed by those of the other hydrocarbons in order. The aromatic series is treated similarly. There can be little doubt that this system is the best in a book which is intended for beginners, and which, hence, can omit mention of many compounds. And herein lies the second advantage of Prof. Pinner's book; while it is full enough, explaining clearly most compounds of practical or theoretical interest, and showing their relations to simpler forms, it attempts no more. The summaries at the end of the different sections are helpful to students. An appendix contains a few pages on stereo-chemistry, on analytical and synthetic methods, on methods for determining constitution and molecular weight, but, singularly enough, makes no mention of the methods of Raoult or Beckmann, which, surely, are simple and important enough to be explained to the student at the close of his course.

E. R.

A HISTORY OF CHEMISTRY, FROM EARLIEST TIMES TO THE PRESENT DAY.  
By Ernst von Meyer. Translated, with the author's sanction, by George  
M'Gowan, Ph. D., Demonstrator in Chemistry, University College of  
North Wales, Bangor. London: Macmillan & Co., 1891.

Prof. v. Meyer's "Geschichte der Chemie" has already been reviewed in this place;<sup>1</sup> it remains but to notice the appearance of the work in English. The fact that Dr. M'Gowan has been a pupil of the author, and that he has already been acknowledged a successful translator, would argue in favor of the value of this book; moreover, the proof-sheets, it is stated, have been revised by Prof. v. Meyer himself.

The style of the original is closely followed throughout, indeed in some ways the book suffers from being a too literal translation. In places Dr. M'Gowan's endeavor to be accurate involves him in the use of expressions which are more German than English, as, for example, in the rendering of compound substantives. This slight defect should not, however, be taken into account, in view of the many excellences which the work evidently possesses.

W. W. R.

## OBITUARY NOTICE.

Dr. VICTOR VON RICHTER, Professor of Chemistry in the University of Breslau, died suddenly October 8. He was born in 1841; studied physics and chemistry at Dorpat, and from 1862 to 1872 was assistant to Mendelejeff in the Technological Institute at St. Petersburg. For a time he was also a teacher in the University of St. Petersburg. In 1872 he accepted a call to the Academy of Agriculture and Forestry at Nowo-Alexandria in Poland. In 1874 he became "Privatdocent" in the University of Breslau, after having spent some time at Bonn with Kekulé. In 1879 he was made professor (*extraordinarius*) in the University, and last year he became professor (*extraordinarius*) of technical chemistry in the new Technological Institute at Breslau.

Richter was widely known for his investigations in the field of organic chemistry, but his name is most familiar as that of the author of the well-known text-books, "Lehrbuch der anorganischen Chemie" and "Chemie der Kohlenstoffverbindungen." Six editions of each of these books have been issued in Germany. They have, further, been translated into English, Dutch, and Italian, and the "Lehrbuch der anorganischen Chemie" into Russian. By these books Richter has contributed materially to the advance of chemistry during the last fifteen years.<sup>2</sup> I. R.

<sup>1</sup> This Journal 11, 429.

<sup>2</sup> For a fuller account of Richter see Chemiker Zeitung 15, No. 82, p. 1495, October 14, 1891.



# AMERICAN CHEMICAL JOURNAL.

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Contributions from the Sheffield Laboratory of Yale University.

## XXXV.—THE DECOMPOSITION OF NITRIC ETHERS BY ALKALINE SOLUTIONS.

BY W. G. MIXTER.

In an examination of a number of high explosives containing some form of gun-cotton or nitrated woody fiber, an attempt was made to prove qualitatively the presence of cellulose nitrate. The substance tested was digested with an alkali sulphide to convert the nitrate into cellulose, then an excess of hydrochloric acid was added, and the mixture boiled for some time to change the cellulose into a sugar having a reducing action on Fehling's solution. The method was not satisfactory, as it was found that gun-cotton and a number of other nitric ethers reduce Fehling's solution directly and without previous treatment with a reducing agent. This observation led to experiments on the decomposition of nitric ethers by alkaline solutions—a line of investigation in which a considerable amount of work has already been done, and in which so much still remains obscure.

### *Ethyl Nitrate.*

According to Millon,<sup>1</sup> ethyl nitrate is decomposed by alcoholic potash, with separation of potassium nitrate free from nitrite. The writer also has found the product to be free from nitrite. Oxalic acid was not formed in the reaction. Ethyl nitrate was heated

<sup>1</sup> Ann. chim. phys. [3] 8, 233.

with Fehling's solution,<sup>1</sup> and also with addition of alcohol to dissolve the ether, and in both experiments there was no reduction of copper.

*Ethylene Nitrate.*

According to Champion,<sup>2</sup> this ether is decomposed by a boiling solution of potassium hydroxide, with formation of ethylene alcohol and potassium nitrate. The decomposition is, however, more complex and not simply a saponification, as the following results show: Ethylene nitrate and concentrated potassium hydroxide were heated together on a water-bath; the change was slight, but on addition of alcohol a violent reaction set in, the solution becoming dark red. A portion of the residue after expelling the alcohol from the solution and adding sulphuric acid, gave off red fumes, showing the presence of considerable nitrite. From the remainder of the residue nitrate was separated, but oxalic acid was not detected. In another experiment ethylene nitrate was decomposed by a boiling solution of potassium hydroxide.<sup>3</sup> The solution obtained on addition of acetic acid and warming gave off carbon dioxide, which formed a considerable precipitate with barium hydroxide. In the product of the decomposition of ethylene nitrate by caustic potash, cyanogen and ammonia were not detected, nor was it found what compounds of carbon other than carbon dioxide were formed. Ethylene nitrate does not reduce Fehling's solution.

A mixture of ethylene nitrate with a solution of barium hydroxide and a little alcohol was heated to boiling; a precipitate slowly formed, consisting in part of barium oxalate. From the solution filtered from the precipitate after removing the barium hydroxide by means of carbon dioxide, a sticky red residue containing nitrite was obtained.

*Nitro-glycerin.*

It is stated in handbooks and dictionaries of chemistry, the new edition of Watts excepted, that nitro-glycerin and caustic potash react to form glycerin and potassium nitrate. This is based on a

<sup>1</sup> The Fehling solution used in all the experiments was made of 173 grams of sodium-potassium tartrate and 125 grams of potassium hydroxide dissolved in water to make 500 cc., and 34.6 grams of crystallised copper sulphate in 500 cc. of water. The two solutions were kept separate until used.

<sup>2</sup> Comptes rend. **73**, 571.

<sup>3</sup> The potassium hydroxide used in this and similar experiments was made from metallic potassium and was free from carbonate.

statement by Williamson<sup>1</sup> and also on an investigation by Railton,<sup>2</sup> both of whom obtained glycerin and potassium nitrate, but made no mention of other products of the decomposition. Later Dr. Matthew Hay<sup>3</sup> made a very good investigation of the action of caustic potash on nitro-glycerin, and showed that the reaction is very complex, and not a simple saponification with formation of glycerin. He found when nitro-glycerin was decomposed by alcoholic potash that two-thirds of the  $\text{—NO}_2$  of the nitro-glycerin was reduced to nitrous anhydride,  $\text{N}_2\text{O}_3$ , and that oxalic acid, a little ammonia and acetic acid were formed. The last may have resulted from oxidation of the alcohol in alkaline solution. Glycerin was not satisfactorily identified as one of the products of the decomposition. The experience of the writer confirms Hay's results in this, that oxalic and nitrous acids and a little ammonia are formed, and that in addition carbon dioxide, nitric acid, and traces of glycerin and cyanogen are among the products of the decomposition of nitro-glycerin by aqueous caustic potash. Organic acids other than oxalic are apparently formed in abundance, but attempts to isolate them have failed. Among the products of the decomposition of nitro-glycerin, glycerose, which is formed by oxidation of glycerin, was tested for with phenylhydrazine, but was not found. The experiments were as follows:

Commercial glycerin, not very pure, was mixed slowly with red fuming nitric acid, cooled by a current of water at  $5^\circ$ , and then oil of vitriol was added gradually. After half an hour the mixture was poured into cold water, and the nitro-glycerin obtained was washed with a solution of sodium carbonate, and finally with water, and dried *in vacuo* over caustic potash. It was colorless, free from acid, and gave on combustion by the absolute method 18.51 per cent. of nitrogen, theory requiring 18.50. This preparation was designated as "A." Another preparation called "B" was made from a purer glycerin known as Price's, and 18.35 per cent. of nitrogen was found in it.

Eight grams of preparation "A" and 50 cc. of potassium hydroxide (density, 1.33) were heated together on a water-bath for some hours until the nitro-glycerin disappeared. A crystalline meal separated, which increased on cooling the mixture. It was filtered off and washed once with cold water, and proved on

<sup>1</sup> Proc. Royal Soc. 7, 130.

<sup>2</sup> J. Chem. Soc. 7, 222.

<sup>3</sup> Trans. Royal Soc. Edin. (1882-3) 32, 67.

analysis to be potassium oxalate. The filtrate from it, on addition of sulphuric acid, gave off nitrous fumes, but glycerin was not detected. Five grams of preparation "B" were decomposed with potassium hydroxide (density, 1.36), and the ammonia evolved was converted into ammonium chloride, which weighed 0.119 gram, showing that  $\frac{1}{30}$  of the nitrogen of the nitro-glycerin had been converted into ammonia. Oxalic acid was estimated as calcium oxalate in  $\frac{1}{6}$  of the solution, and the result showed that  $\frac{1}{18}$  of the carbon of the nitro-glycerin was converted into oxalic acid. From the remaining  $\frac{5}{6}$  of the solution potassium nitrate was obtained, but no glycerin.

In order to test more thoroughly for glycerin in the products of decomposition, much larger quantities of nitro-glycerin were used. In one experiment 24 grams of preparation "A" were decomposed by 115 cc. of potassium hydroxide (density, 1.4), and the salts which separated were removed. Carbon dioxide was then passed into the solution as long as hydrogen-potassium carbonate separated, and this was filtered off and washed with alcohol. The filtrate and washings were evaporated until a viscid mass remained, which was shaken up with alcohol; the solution poured off from the undissolved salts was evaporated, and the residue left was also extracted with alcohol. This last solution yielded a viscid product which gave a feeble but distinct odor of acrolein when heated with phosphorus pentoxide. 32 grams of preparation "B," treated as just described, also reacted for a trace of glycerin. In order to test the method employed, 10 grams of potassium nitrite, 2 grams of oxalic acid, and 0.5 gram of glycerin were added to a solution of caustic potash, and the mixture was treated as above described. Glycerin was found in much larger quantity than in the foregoing tests.

Nitro-glycerin of preparation "A" was decomposed by an aqueous solution of pure potassium hydroxide, and the solution was found to give off carbon dioxide on the addition of an acid. No gas was obtained when nitro-glycerin was decomposed *in vacuo* by pure concentrated potassium hydroxide, and the solution reacted for a trace of cyanogen.

Nitro-glycerin dissolves in a hot Fehling solution, and cuprous oxide continues to separate long after the oily drops of the ether have disappeared, showing that reducing compounds are gradually formed by the action of the alkali. The reducing bodies are,

however, decomposed by the alkali, for when nitro-glycerin is first dissolved in concentrated potassium hydroxide and Fehling's solution then added, no reduction occurs. But if the decomposition is effected by barium hydroxide, the reducing compound is not destroyed. 30 grams of nitro-glycerin were added to a boiling solution of 150 grams of barium hydroxide in 600 cc. of water, and the boiling was continued half an hour. Ammonia came off and a reddish precipitate separated, which was washed with water and finally with alcohol to remove any adhering nitro-glycerin. This precipitate reduced Fehling's solution, and gave off ammonia when heated with lime. It was treated with acetic acid, and the undissolved portion proved on analysis to be barium oxalate. The acetic acid solution was evaporated until a crystalline crust formed, which gave analytical results indicating a mixture, doubtless containing oxalate. In another experiment the precipitate obtained as before was digested with the amount of sulphuric acid required to remove the barium. The filtrate from the barium sulphate did not yield crystals on evaporation, and when treated with phenyl-hydrazine hydrochlorate, sodium acetate and acetic acid, a dark-red sticky precipitate formed, which was apparently a product of the decomposition of phenyl-hydrazine. The filtrate from the precipitate formed in the reaction between the barium hydroxide and nitro-glycerin contained nitrite and nitrate and organic matter.

*Nitro-mannite.*

30 grams of this compound were gradually added to a boiling, clear solution of 100 grams of barium hydroxide in a liter of water, and the boiling was maintained for an hour. No ammonia was detected in the escaping steam. The decomposition of the nitro-mannite was accompanied by the formation of a red granular precipitate, which was filtered off and thoroughly washed with hot water. It was evidently a mixture, as it contained barium oxalate and reduced Fehling's solution. It was treated with a slight excess of dilute sulphuric acid, and to the filtrate from the barium sulphate, phenyl-hydrazine hydrochlorate, sodium acetate, and acetic acid were added to separate, if possible, any ketonic acid or compound which reduces copper. A dark-red precipitate formed at once, which increased on warming and standing. It was insoluble in alcohol, the solution yielding only a tarry mass when evaporated. The filtrate from the phenyl-hydrazine product, on evaporation and cooling, deposited crystals of phenyl-hydrazine oxalate.



The filtrate from the red precipitate produced by the reaction between nitro-mannite and barium hydroxide, was treated with carbon dioxide to remove barium hydroxide. The solution filtered from the barium carbonate contained barium nitrite in abundance, and also nitrate. It did not reduce Fehling's solution, nor yield a precipitate with lead acetate. It left a residue on evaporation, which deflagrated, thus showing the presence of carbon compounds.

Nitro-mannite is easily decomposed by a hot solution of potassium hydroxide; if the solution be concentrated, oxalic acid is formed. When a very dilute solution of the alkali was used, no oxalic acid was detected. In one experiment, about  $\frac{1}{10}$  of the carbon of nitro-mannite was converted into carbon dioxide, when the ether was decomposed by concentrated potash solution. The product of the decomposition of nitro-mannite by a strong solution of potassium hydroxide does not reduce Fehling's solution; but if the alkali be dilute, the solution has a slight reducing action. When, however, nitro-mannite is added to Fehling's solution, there is considerable reduction. Two estimations were made with 0.5 gram of nitro-mannite and 50 cc. of Fehling's solution, and, after boiling three-quarters of an hour, 0.1356 and 0.130 gram of metallic copper respectively were obtained. After boiling an hour longer, the total amount of copper precipitated was 0.196 and 0.199 gram respectively.

#### *Cellulose Nitrates.*

The action of caustic potash on pyroxylin has been investigated by Béchamp<sup>1</sup> and by Eder.<sup>2</sup> The former states that if pyroxylin be heated with a solution of caustic potash, and the action be stopped just before a stage in the decomposition is reached where acids fail to produce a precipitate, and the solution is exactly neutralised with dilute sulphuric acid, it is possible to prove the formation of a sugar. For this, the solution is evaporated on a water-bath and extracted with hot alcohol. The alcohol leaves a saline residue of sulphate, nitrate and nitrite, and holds in solution a certain quantity of sugar. The sugar product was fermented and alcohol obtained. The writer has repeatedly sought by means of phenyl-hydrazine for a sugar, and found none among the products of decomposition of pyroxylin, by dilute solutions of caustic potash. The pyroxylin used was a commercial article,

<sup>1</sup>Ann. chim. phys. [3], 46, 338.

<sup>2</sup>Ber. d. chem. Ges. 13, 169.

soluble in ether-alcohol, and had the composition of cellulose tetranitrate,  $C_{12}H_{10}(NO_3)_4O_{10}$ , doubtless containing tri- and pentanitrates. The method employed was as follows: 28 grams of pyroxylin were placed in 500 cc. of water, to which from 40 to 70 cc. of potassium hydroxide (density, 1.4) had been added. The mixture was heated until most of the pyroxylin had dissolved, then cooled, and a slight excess of either sulphuric or hydrochloric acid added, an excess being required to completely precipitate a small quantity of undecomposed cellulose nitrate. The solution was filtered, exactly neutralised with potassium hydroxide, and evaporated nearly to dryness on a water-bath. The saline residue, after washing two or three times with alcohol, which removed but little organic matter, blackened on ignition and reduced Fehling's solution. It was dissolved in a small quantity of water, and phenyl-hydrazine hydrochlorate, sodium acetate and acetic acid were added. A yellow precipitate separated, which turned red on warming the solution, and was apparently a decomposition-product of phenyl-hydrazine. In one experiment, a sparingly soluble potassium salt, not the oxalate, was obtained. Repeated attempts to prepare more of the salt failed.

While working with phenyl-hydrazine, as just described, the writer's hand was repeatedly blistered by vapors and by solutions. No poisonous effects were, however, noticed after experimenting with phenyl-hydrazine and the products of decomposition by alkalis of nitric ethers other than pyroxylin. At some future time the writer will endeavor to identify the poisonous compound.

Eder<sup>1</sup> states that alkalis decompose pyroxylin with formation of nitrites and nitrates, but little nitrate being formed when dilute alcoholic potash is used. Béchamp<sup>1</sup> found that glucic and apoglucic acids resulted from prolonged action of concentrated potash. The writer finds that oxalic and carbonic acids are formed when pyroxylin is decomposed by a strong solution of caustic potash, and the product does not reduce Fehling's solution. A solution of pyroxylin in dilute caustic potash has, however, some reducing action.

Pyroxylin dissolves quickly in a hot Fehling solution, and cuprous oxide separates at once, but the reduction continues for a long time. In two estimations, using for each 0.5 of soluble pyroxylin and 50 cc. of Fehling's solution and boiling three hours,

<sup>1</sup> Loc. cit.

0.375 and 0.365 gram respectively of copper were precipitated as cuprous oxide. 0.5 gram of another sample of pyroxylin gave 0.4 gram of copper on boiling an hour, and 0.44 gram at the end of two hours, 50 cc. of Fehling's solution being used.

In another test with 0.5 gram of the same sample, and 50 cc. of Fehling's solution diluted with its bulk of water, only 0.25 gram of copper was precipitated, and no further reduction occurred after boiling an hour. There was an undetermined error in using Fehling's solution undiluted, as it deposited a small amount of cuprous oxide when boiled for some time. A specimen of gun-cotton which was nearly pure cellulose hexanitrate reduced about half as much copper from an undiluted Fehling's solution as pyroxylin under like conditions.

#### *Other Nitric Ethers and Reducing Compounds.*

The following substances are converted by concentrated nitric acid into compounds which precipitate cuprous oxide from Fehling's solution: Pinite, woody fiber, gum arabic, gum tragacanth, balsam of tolu, glycogen, starch and saccharose. The nitrated products of blood-albumen, hard-boiled white and yolk of egg, caoutchouc, tartaric acid, beeswax and tallow were found to be without reducing action.

#### *Summary.*

Ethyl nitrate and potassium hydroxide react to form ethyl alcohol and potassium nitrate, and there is no reduction of the  $\text{NO}_2$ -group or oxidation of the ethyl-group. Ethylene nitrate is decomposed by concentrated alkaline solutions with formation of carbonic, oxalic, and nitrous acids, part of the oxygen of the  $\text{NO}_2$ -groups oxidising the hydrocarbon radicle. Nitro-glycerin, nitro-mannite, and pyroxylin exhibit a similar deportment, and in addition yield other organic acids and products which have a reducing action on Fehling's solution.

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### XXXVI.—RESEARCHES ON THE ISO-ANILIDES.

BY W. J. COMSTOCK AND H. L. WHEELER.

In the first part of this paper we shall describe experiments which show that the sodium and silver salts of form-*a*-naphthalide and of metanitro-formanilide show, in their behavior towards methyl iodide, the same difference that has been found in the salts

of other aromatic formyl compounds. The second part contains a description of experiments made with the iso-anilides, showing that they react with secondary amines, both fatty and aromatic, and with cyan-amide.

Gattermann<sup>1</sup> made the interesting observation that nitro-para-acetoluide occurs in two modifications, and suggested the possibility that these two modifications might correspond to the forms containing the two groups  $\text{—N}=\text{C}(\text{OH})\text{—}$  and  $\text{—NH—CO—}$ . It seemed possible that in the case of nitro-formanilide—whose salts behave towards methyl iodide as if they had the structures  $\text{—NNa—CO—}$  and  $\text{—N}=\text{C}(\text{OAg})$  respectively—these two modifications might be obtained by decomposing the salts. But we were able to obtain but a single modification of the meta-nitro-formanilide in this way. The decomposition of both salts by dry hydrochloric acid in presence of dry ether and in presence of dry chloroform; the decomposition of the silver salt by dry hydrogen sulphide in presence of dry ether; and the decomposition of the sodium salt by moist carbonic acid in presence of ether; all gave products having the same melting-point. In each case, on evaporating the solution at ordinary temperature, the crystals had exactly the same appearance under the microscope, consisting of tufts of extremely fine, hair-like, bent needles. Under these conditions we could not, however, obtain crystals that were fitted for crystallographical or optical examination.

*Silver salt of form-a-naphthalide.*—Prepared by adding gradually the theoretical quantity of silver nitrate in 50 per cent. alcoholic solution to the aqueous alcoholic solution of sodium hydroxide and the formyl compound. The silver salt separates as a voluminous gray precipitate, amorphous and sensitive to light, insoluble in water.

	Found.	Calculated.
Ag	39.14	38.84

*Methyl-iso-form-a-naphthalide.*—Prepared by treating the dry silver salt with methyl iodide in presence of dry ether, this compound is obtained as a heavy oil, having a strongly fishy odor, and boiling at ordinary pressure, with noticeable decomposition at  $306^{\circ}\text{--}308^{\circ}$ .

	Found.	Calculated.
C	77.8	77.7
H	5.9	6.0

<sup>1</sup> Ber. d. chem. Ges. 23, 1733.

It shows the same behavior towards water, dilute acids and primary amines, that methyl-iso-formanilide does.

*Di- $\alpha$ -naphthyl-formamidine*.—Formed by treating the above-described ether with  $\alpha$ -naphthylamine, and recrystallising from hot benzene. It forms colorless plates, which melt at  $199^{\circ}$ , and are moderately soluble in alcohol, ether and benzene, insoluble in ligroin. Does not dissolve in cold, dilute mineral acids.

	Found.	Calculated.
C	85.2	85.1
H	5.5	5.4
N	9.4	9.5

*Phenyl- $\alpha$ -naphthyl-formamidine*, prepared by treating methyl-iso-form- $\alpha$ -naphthalide with aniline, is purified by dissolving in benzene and precipitating with ligroin. Its melting-point is  $142^{\circ}$ . It is soluble in alcohol, ether and benzene, difficultly soluble in ligroin.

	Found.	Calculated.
C	83.3	82.9
H	5.8	5.7
N	11.3	11.4

The basic properties are much more strongly marked than in the case of the dinaphthyl-amidine.

The reaction of methyl iodide with the sodium salt of form- $\alpha$ -naphthalide is not a satisfactory operation, owing to the properties of the methyl-naphthyl-amine. However, by Hepp's method, we obtained the base corresponding to that described by Landshoff.<sup>1</sup> An attempt to purify it by means of the nitrosamine was a failure, as nitrous acid seemed to have a more complicated action, and left a most uninteresting resinous product. However, by means of the acetyl compound described by Landshoff, we were able to identify the secondary amine.

*Meta-nitro-formanilide*.—This is easily prepared by boiling meta-nitraniline with an excess of pure formic acid, adding water and recrystallising from hot water, alcohol or benzene. It melts at  $134^{\circ}$ . It is soluble in hot water, alcohol and benzene; difficultly soluble in ether and ligroin.

	Found.	Calculated.
C	50.6	50.6
H	3.9	3.6

<sup>1</sup> Ber. d. chem. Ges. **11**, 638.



*Sodium meta-nitro-formanilide.*—To prepare the sodium salt, the best method is to dissolve the theoretical quantity of sodium in the smallest possible quantity of pure, dry methyl alcohol, and add it to the formyl body, which has been moistened to a paste with methyl alcohol. The lemon-yellow salt which is formed is readily soluble in methyl alcohol, and should be washed thoroughly with dry ether. A sodium estimation in the salt thus prepared gave  $\text{Na} = 12.1$  per cent. (calculated,  $\text{Na} = 12.2$  per cent.). Exposed to the air the salt gradually absorbs carbonic acid, and is finally completely converted into sodium carbonate and the formyl compound. If in preparing the sodium salt the methyl alcohol is not thoroughly washed out by ether, the lemon-yellow salt gradually changes into a mass of orange-colored needles, which, dried over sulphuric acid, gave  $\text{Na} = 10.1$  per cent. The theoretical percentage for the sodium salt with one mol.  $\text{CH}_3\text{OH}$  is  $\text{Na} = 10.45$ . The same orange-colored needles are obtained when the alcoholic solution is concentrated. On adding water to the alcoholic solution of the salt, the free formyl compound is precipitated.

*Action of methyl iodide on the sodium salt.*—Methyl iodide reacts but slowly with the sodium salt when warmed on the water-bath in a flask fitted with an inverted condenser; nevertheless the reaction can be made to take place in this way if the heating be continued for some days, care being taken to exclude moisture and carbonic acid.

The reaction is finished when a specimen of the mixture no longer shows an alkaline reaction. The reaction takes place in a very few hours when conducted in a sealed tube at  $100^\circ$ . In either case, by crystallising from alcohol, the nitro-formyl-methyl-aniline can be obtained in long needles, having a slight yellowish tinge and melting at  $70^\circ$ – $71^\circ$ .

	Found.	Calculated.
C	53.0	53.3
H	4.5	4.4

The meta-nitro-monomethyl-aniline prepared from the pure formyl compound melted at  $67^\circ$ , and the nitrosamine, which we obtained perfectly white, melted at  $76^\circ$ . Nölting and Stricker<sup>1</sup> gave  $65^\circ$ – $66^\circ$  and  $68^\circ$ – $70^\circ$  as the melting-points of these two compounds.

*Silver meta-nitro-formanilide.*—The silver salt can be prepared

<sup>1</sup> Ber. d. chem. Ges. 19, 548.

in aqueous-alcoholic solution in the same manner as silver form-anilide. It is amorphous, and, when first precipitated, colorless. It can be washed with hot water.

	Found.	Calculated.
Ag	39.8	39.3

*Meta-nitro-methyl-iso-formanilide* is prepared by treating the dry silver salt with methyl iodide diluted with ether. On fractioning at a pressure of 21 mm., the iso-anilide was obtained, boiling at 172°–173°; temperature of bath, 190°. The compound solidifies in the receiver to a mass of long, slender, light-yellow needles, melting at 45°.

	Found.	Calculated.
C	53.5	53.3
H	4.5	4.4
N	15.8	15.6

The ether reacts with primary amines, as do the others thus far described, but the tendency to form the amidine in presence of water is not so marked as in the case of the non-substituted iso-anilides. Treated with dilute hydrochloric acid, for instance, the salt of meta-nitraniline is obtained at once.

*Dinitro-diphenyl-formamidine*,  $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_4.\text{NO}_2 \\ \diagdown \text{NH.C}_6\text{H}_4.\text{NO}_2 \end{smallmatrix}$ .—A mixture of the theoretical quantities of the iso-anilide and meta-nitraniline, heated up slowly on a bath, remained liquid from 50° to about 110°, at which temperature the mass became solid. On recrystallising from alcohol, the amidine was obtained in small yellow hair-like needles, melting at 195°–196°. A combustion of the substance dried at 130° gave the following results:

	Found.	Calculated.
C	54.9	54.5
H	3.6	3.5

The compound is soluble in alcohol, ether, chloroform, and acetone; insoluble in ligroin.

*Mono-nitro-diphenyl-formamidine*,  $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_4.\text{NO}_2 \\ \diagdown \text{NH.C}_6\text{H}_5 \end{smallmatrix}$ .—On adding the theoretical quantity of aniline to the fused ether, the mixture solidifies in a few minutes, and when crystallised from absolute alcohol the amidine is obtained in long yellow prisms which melted at 145°.

	Found.	Calculated.
C	64.8	64.7
H	4.7	4.6

The following experiments will serve to show that the iso-anilides react with secondary amines, fatty and aromatic, forming tri-substituted amidines:

*Diethyl-phenyl-formamidine*,  $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_5 \\ \diagdown \text{N}(\text{C}_2\text{H}_5)_2 \end{smallmatrix}$ .—A mixture of methyl-iso-formanilide and a slight excess of diethyl-amine was boiled in a flask fitted with an inverted condenser for about two hours, and then distilled at ordinary pressure. Practically the entire quantity came over between  $265^\circ$  and  $275^\circ$ . On redistilling, a nearly colorless oil was obtained, boiling at  $273^\circ$ – $275^\circ$ . There was, however, a noticeable decomposition, and the compound had a strongly alkaline odor. Converted into the gold double-salt and recovered, the amidine is colorless and odorless. The gold double-salt is difficultly soluble in water, easily soluble in alcohol, and crystallises in small lemon-yellow plates when water is added to the alcoholic solution; the plates melt at  $147^\circ$ . After drying over sulphuric acid *in vacuo*, its analysis gave the following results:

	Found.	Calculated for $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_5 \\ \diagdown \text{N}(\text{C}_2\text{H}_5)_2 \end{smallmatrix} \cdot \text{HCl} + \text{AuCl}_3$ .
C	25.9	25.6
H	3.5	3.3
N	5.4	5.4
Au(=196.6)	37.9	38.1

*Methyl-diphenyl-formamidine*,  $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_5 \\ \diagdown \text{N} < \text{CH}_3 \\ & \text{C}_6\text{H}_5 \end{smallmatrix}$ .—A mixture of monomethyl-aniline and methyl-iso-formanilide was allowed to stand at ordinary temperature for some days, and, after having been warmed on the water-bath a short time, was distilled under diminished pressure: an excellent yield of the amidine was obtained. The substance is a heavy yellowish oil, boiling at  $214^\circ$  under 22 mm. pressure; temperature of bath,  $260^\circ$ .

	Found.	Calculated.
C	79.6	80.0
H	6.7	6.7
N	13.5	13.3

The gold double-salt is difficultly soluble in water, and when water is added to the alcoholic solution crystallises in gold-colored

plates which melt at  $145^{\circ}$ . A gold estimation in the air-dried salt gave  $\text{Au} = 35.7$  per cent.; calculated for the anhydrous salt,  $\text{Au} = 35.7$  per cent.

*Action of Cyan-amide on the Iso-anilides.*

*Cyan-phenyl-formamidine*,  $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_5 \\ \diagdown \text{N.H.CN} \end{smallmatrix}$ .—When an ethereal solution of cyan-amide and methyl-iso-formanilide is allowed to stand at ordinary temperature, it soon begins to deposit a crystalline crust, the separation of which is practically complete in 24 hours, unless the solution is very dilute. The new compound, after washing with ether, can be recrystallised from hot water or alcohol, in both of which it is quite soluble. From alcohol it separates in long, flat, colorless prisms; from hot water, in long needles. Its melting-point is  $138^{\circ}$ . Its analysis corresponds to the formula  $\text{C}_8\text{H}_7\text{N}_3$ , and its structure is in all probability represented by the formula  $\text{CH} \begin{smallmatrix} \diagup \text{N.C}_6\text{H}_5 \\ \diagdown \text{N.H.CN} \end{smallmatrix}$ .

	Found.	Calculated.
C	66.0	66.2
H	5.0	4.8
N	29.0	29.0

*Cyan-para-tolyl-formamidine*.—Cyan-amide reacts with methyl-iso-form-para-toluide in ethereal solution in the same way that it does with the iso-anilide. Recrystallised from alcohol the new body is obtained in long, well-developed prisms which melt at  $176^{\circ}$ – $177^{\circ}$ .

	Found.	Calculated.
C	68.0	67.9
H	5.7	5.6
N	26.3	26.4

### XXXVII.—ON THE PREPARATION OF OXYGEN-ETHERS OF SUCCINIMIDE FROM ITS SILVER SALT.

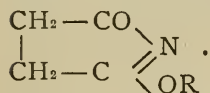
BY W. J. COMSTOCK AND H. L. WHEELER.

The action of ethyl iodide on silver succinimide has already been tried by Menschutkin,<sup>1</sup> as well as by Landsberg,<sup>2</sup> in the

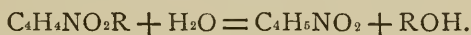
<sup>1</sup> Ann. Chem. (Liebig) 162, 170.

<sup>2</sup> Ibid. 215, 211.

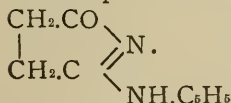
course of his extended investigation on the imides of dibasic acids. Both investigators state that they obtained only silver iodide and regenerated succinimide. Comstock and Kleeberg<sup>1</sup> found that by treating dry silver succinimide with methyl iodide, at most a trace of succinimide was regenerated; but they did not obtain the resulting compound in a pure state. That it was not the well known methyl succinimide, *i. e.*, the nitrogen-ether of succinimide, was shown by the fact that it reacted with aniline, with the formation of the base to be described later. We have taken up the work at this point and succeeded in preparing in a state of purity the ethyl and propyl compounds resulting from the action of the corresponding iodides on silver succinimide. These compounds were found to be isomeric with the nitrogen ethers of succinimide, and have, without doubt, the structure



We have not attempted to prepare the corresponding methyl-derivative, as its boiling-point was found by Kleeberg to be too near that of the nitrogen-ether to allow a separation by fractional distillation, in case any nitrogen-ether should be formed in the reaction. It is absolutely essential in preparing the oxygen-ethers, to exclude all moisture, even after the reaction is over, as the pure bodies form succinimide when exposed to moist air:



This ready formation of succinimide from the oxygen-ethers explains Landsberg's failure to obtain anything but silver iodide and succinimide when he allowed ethyl iodide to act on the dry silver salt in presence of dry benzene. We have found that the oxygen-ethers are formed in presence of dry benzene, ether or chloroform, the last being used in conducting the reaction with larger quantities. The formation of the oxygen-ether can readily be detected after filtering from the silver iodide, by evaporating the solvent and adding a few drops of aniline. The base formed has the composition  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$ , and has without doubt the formula



<sup>1</sup> Ber. d. chem. Ges. 23, 2274; This Journal 12, 493.



Succinimide is thus placed in the category with formanilide and other formyl compounds of primary aromatic amines, since it was shown by Landsberg that the alkaline salts give the nitrogen-ethers when treated with alkyl iodides. We were also able to show that in each case a small quantity of the nitrogen-ether had been formed from the silver salt. This was done by decomposing the ethers with a solution of potassium hydroxide, and showing the presence of a primary amine by the iso-nitrile reaction. This formation of a small quantity of nitrogen-ether from the silver salt renders the assumption of a different structure for the sodium and silver salts less satisfactory, as in that case refuge must be taken in the assumption of a molecular rearrangement at low temperature. We have attempted to find experimental evidence that might throw more light on this interesting subject, but as our results have been thus far negative, we present the definite experimental results already obtained and postpone the discussion of the theory till a future date.

*Oxygen-ethyl-succinimide.*—Silver succinimide dried to a constant weight at  $100^{\circ}$  was allowed to stand for several weeks at ordinary temperature with the theoretical quantity (1 mol.) of ethyl iodide diluted with two to three times its weight of dry chloroform. After filtering off the silver iodide and washing with more dry chloroform, the chloroform was distilled off on the water-bath, and the dark, oily residue distilled under diminished pressure. A second distillation yielded the oxygen-ether as a colorless oil, boiling at  $144^{\circ}$ – $146^{\circ}$  under a pressure of 20 mm., the temperature of the bath being  $190^{\circ}$ . The compound decomposes when boiled at ordinary pressure, and even at 20 mm. a slight decomposition can be noticed. Analysis gave results agreeing with the theory.

	Found.	Calculated for $C_8H_9NO_2$ .
C	56.62	56.69
H	7.11	7.09

On adding aniline the mixture solidifies at once, and with noticeable evolution of heat if more than a few drops are used in the reaction. When exposed to moist air the pure ether gradually solidifies, forming succinimide, which shows the correct melting-point without recrystallisation. In order to test for the presence of the nitrogen-ether, a small quantity of the chloroform solution, representing about six to eight grams of silver salt freshly filtered from silver iodide, was treated with water and allowed to stand

several hours after vigorous shaking. The chloroform was then distilled off, the aqueous solution distilled with potassium hydroxide, and an examination for primary amine made in the way described under the propyl-ether. The presence of a primary amine was shown beyond doubt, therefore some nitrogen-ether had been formed in the reaction. If the nitrogen-ether is formed by molecular rearrangement from the oxygen-ether, that rearrangement must take place in this case at ordinary temperature, as the oxygen-ether must have been completely converted into succinimide by the action of the water before any heat was applied. The nitrogen-ethyl-ether, which was prepared for comparison according to Menshutkin, boiled at  $235^{\circ}$  at 763 mm. pressure (Menschutkin gives  $234^{\circ}$ ), and at 20 mm. showed the boiling-point  $122^{\circ}$ ; temperature of bath,  $155^{\circ}$ . It does not react with aniline.

*Oxygen-propyl-succinimide.*—This was prepared in the same way as the corresponding ethyl-compound, but the reaction took place more slowly. After five weeks the chloroform solution was filtered from the iodide, and it was found that a noticeable quantity of silver iodide separated on evaporating the solution, so that the residue was again taken up in chloroform and treated as described under the ethyl-ether. At the first distillation it was found that at 19 mm. pressure but a few drops came over below  $153^{\circ}$ , while almost the entire quantity boiled between  $153^{\circ}$  and  $160^{\circ}$ . On redistilling, the greater part came over at  $153^{\circ}$ – $154^{\circ}$  (pressure, 19 mm.; temperature of bath,  $195^{\circ}$ ), again leaving a dark residue.

Analysis gave the following results:

	Found.	Calculated for $C_7H_{11}NO_2$ .
C	59.10	59.57
H	7.95	7.80
N	10.30	9.92

The slight variation of our results from the theory would indicate the presence of a small quantity of succinimide, but as its boiling-point must be very close to that of the ether, a separation would hardly be possible, and is indeed not necessary. Like the corresponding ethyl-ether, it decomposes when boiled at ordinary pressure; gives succinimide when exposed to the air, and reacts at once with aniline. As the nitrogen-propyl-ether has a lower boiling-point than the oxygen-ether, the first portions of the distillate from the impure oxygen-ether were examined for the nitrogen-ether. It was impossible, from the boiling-points

given, that more than a small quantity of nitrogen-ether could be present, and this could hardly be separated in a pure state. So the first portions of the distillate were boiled with a strong solution of potassium hydroxide as long as any volatile base came off, the volatile part being caught in dilute hydrochloric acid. On evaporating the acid solution it was found from its insolubility in cold absolute alcohol, that the greater part of the residue consisted of ammonium chloride, but that in that portion soluble in alcohol we could positively identify propylamine by the iso-nitrile reaction. Therefore a small quantity of the nitrogen-ether is formed together with the oxygen-ether.

*Nitrogen-propyl-succinimide.*—For comparison we prepared this compound by the same method that Menschutkin used in making the methyl- and ethyl compounds—by distilling the acid succinate of propylamine. We obtained it as a colorless oil boiling at  $247^{\circ}$ – $248^{\circ}$  at 763 mm. pressure. When cooled in a freezing-mixture it solidifies and shows the melting-point  $15^{\circ}$ – $16^{\circ}$ . It boiled at  $136^{\circ}$ – $137^{\circ}$  at 27 mm. pressure. It does not form the base  $C_{10}H_{10}N_2O$  with aniline. A nitrogen estimation gave N 9.92 per cent.; the theory requires 9.80 per cent.

*Base  $C_{10}H_{10}N_2O$ .*—This base is formed at once, as we have before stated, on adding aniline to one of the oxygen-ethers of succinimide. If the ether be pure the resulting base needs only to be recrystallised from alcohol. If an impure ether be used, the base can be readily purified by dissolving it in cold dilute hydrochloric acid, filtering from the dark residue and precipitating with ammonia. Its melting-point is  $216^{\circ}$ . It crystallises from hot alcohol, on cooling rapidly, in small, transparent, quadrilateral plates. Dried at  $100^{\circ}$  its analysis gave the following results:

	Found,	Calculated for $C_{10}H_{10}N_2O$ .
C	69.36	68.96
H	5.79	5.74
N	16.20	16.09

The gold double-chloride of the base is precipitated from the acid solution on adding gold chloride. When prepared in the cold the double-salt forms a voluminous, sulphur-yellow precipitate consisting of microscopic needles. When the gold-chloride solution is added to the hot acid solution of the base, the double-salt separates on cooling in gold-yellow prisms. The salt should not

stand long in contact with the mother-liquor; even when filtered quickly and dried *in vacuo* over sulphuric acid, it turns green on the surface. A gold estimation gave  $\text{Au} = 38.46$  per cent.; calculated for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O} \cdot \text{HCl} \cdot \text{AuCl}_3$ ,  $\text{Au} (= 196.6) = 38.38$ . The salt melts with decomposition at  $170^\circ$ .

### XXXVIII.—ON SOME DERIVATIVES OF AROMATIC FORMYL COMPOUNDS.

BY W. J. COMSTOCK AND R. R. CLAPP.

The curiously different behavior of the sodium and silver salts of formanilide towards methyl iodide, as shown by Comstock and Kleeberg,<sup>1</sup> is of especial interest as the first case of a compound containing the group  $\text{—NH—CO—}$  [or  $\text{—N=C(OH)—}$ ], whose sodium salt yields, under conditions which exclude dissociation, the nitrogen-ether—*i. e.* formyl-monomethyl-aniline,—while the silver salt gives the oxygen-ether—*i. e.*, methyl-iso-formanilide,

$\text{C}_6\text{H}_5\text{N}=\text{C} \begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix} \text{CH}_3$ . We have continued the experiments in that direction and found that form-ortho-toluide and form-para-toluide behave in the same way: both give silver salts which, on treatment with methyl iodide, yield iso-toluides; and the sodium salt of each can be used for preparing the secondary amine. As a contribution to our knowledge of the iso-anilides, we have also prepared seven higher ethers and found that they give the same reactions,—formation of diphenyl-form-amidine by the action of aniline, by the action of a dilute acid, and by the gradual absorption of water on exposure to the air. We have also found, though without purifying and analysing the products, that methyl-iso-formanilide reacts with other primary aromatic amines as well as with aniline; and have prepared and analysed the amidines formed by treating it with hydroxyl-amine and benzyl-amine. On decomposing the silver salt of form-para-toluide in presence of dry ether with dry hydrochloric acid gas or with dry hydrogen sulphide—care being taken to have the silver salt in excess,—we found on evaporating the ether at ordinary temperature under diminished pressure, that the residue fused at  $52^\circ$ , as did also a specimen of pure form-para-toluide attached to the same thermometer. Nor could we observe, as the compound crystallised from ether, any

<sup>1</sup> This Journal 12, 493.

difference in crystalline form which could warrant the assumption that an isomer had first been formed and afterwards transformed during the heating into the more stable ordinary form-para-toluide. This suggests the similar behavior of silver benzamide<sup>1</sup> towards hydrochloric acid and hydrogen sulphide; although with methyl iodide it gives the imido-ether  $\text{C}_6\text{H}_5.\text{C} \begin{smallmatrix} \diagup \text{O}.\text{CH}_3 \\ \diagdown \text{NH} \end{smallmatrix}$ . In the case of benzamide, however, the sodium salt could not be prepared. In form-para-toluide we have therefore a case in which sodium and silver salts regenerate the same mother-substance, while they behave differently towards methyl iodide. As we have been unable to find any experimental proof, either of the existence in the free state of an isomeric form-para-toluide, or that in treating the salts with iodides anything beyond a direct replacement of metal by alkyl occurs, the best explanation seems to be that the salts have a different structure, while only one form of the free formyl compound is capable of existing. Possibly in some of the compounds belonging to this class it will be found that both forms are capable of existing.

*Derivatives of form-ortho-toluide and form-para-toluide.*—The silver salts of both these compounds can be made by exactly the same method as was used in preparing silver formanilide. The preparation of the iso-form-toluides from the silver salts is exactly like the preparation of methyl-iso-formanilide, and they show the characteristic behavior of the latter compound. The two amidines were made from the iso-toluides by the action of the corresponding toluidines.

*Silver form-ortho-toluide* is amorphous and sensitive to light; it is insoluble in cold water.

	Found.	Calculated.
Ag	44.37	44.63

*Methyl-iso-form-ortho-toluide* is an aromatic oil boiling at  $211^\circ$ – $213^\circ$  at 760 mm. pressure.

	Found.	Calculated for $\text{C}_9\text{H}_{11}\text{NO}$ .
C	72.42	72.48
H	7.38	7.38
N	9.71	9.39

*Di-ortho-tolyl-formamidine*, when recrystallised from alcohol, melted at  $150^\circ$ .

<sup>1</sup> Tafel and Enoch; Ber. d. chem. Ges. 23, 103.



	Found.	Calculated for $C_{15}H_{16}N_2$ .
C	80.30	80.36
H	7.9	7.14

This compound has already been made by Ladenburg<sup>1</sup> and by Senier<sup>2</sup> by other methods.

*Silver form-para-toluide* was obtained as a voluminous precipitate consisting entirely of small needles, practically insoluble in cold water; sensitive to light.

	Found.	Calculated.
Ag	44.98	44.63

*Methyl-iso-form-para-toluide* is an aromatic oil boiling at  $216^{\circ}$ – $218^{\circ}$  at 761 mm. pressure.

	Found.	Calculated for $C_9H_{11}NO$ .
C	72.44	72.48
H	7.54	7.38
N	9.56	9.39

*Di-para-tolyl-formamidine*, when purified by crystallisation from pure benzene—from which it separates in flat, transparent, colorless prisms of considerable size—melts at  $140^{\circ}$ .

	Found.	Calculated for $C_{15}H_{18}N_2$ .
C	80.45	80.36
H	7.21	7.14
N	12.60	12.50

This amidine was also prepared by Senier.<sup>3</sup>

In trying the behavior of the sodium salts of both formyl compounds towards methyl iodide, we found that the monomethyl-toluidines could be prepared either by following Hepp's method for the preparation of monomethyl-aniline, or by using sodium methylate and methyl iodide in presence of dry methyl alcohol. The yield is better when Hepp's method is followed, in which case benzene can be used in place of xylene, although the action of the sodium is then much slower. The secondary base was, however, in no case obtained absolutely pure until converted into the nitroso-compound and recovered. Monomethyl-ortho-toluidine boiled at  $280^{\circ}$ ; the para-compound at  $211^{\circ}$ – $212^{\circ}$ .

*Ethyl-iso-formanilide* is an aromatic oil boiling at  $213^{\circ}$ – $215^{\circ}$  at 761 mm. pressure.

<sup>1</sup> Ber. d. chem. Ges. **10**, 1260.

<sup>2</sup> Ibid. **18**, 2294.

<sup>3</sup> Loc. cit.

	Found.	Calculated for $C_9H_{11}NO$ .
C	72.57	72.48
H	7.60	7.38

*Propyl-iso-formanilide* boils at  $233^{\circ}$ – $235^{\circ}$  at 760 mm. pressure.

	Found.	Calculated for $C_{10}H_{13}NO$ .
C	73.39	73.62
H	8.24	7.98

Both of these ethers react, as before stated, exactly like the methyl-ether.

*Phenyl-benzyl-formamidine*.—Benzyl-amine and methyl-iso-formanilide react slowly in the cold when mixed in molecular proportions. The solid crystalline product, after being pressed free from a small quantity of oil, can be recrystallised by dissolving in strong alcohol and adding water until a permanent turbidity results. The base comes down oily at first, but gradually solidifies, forming colorless, transparent, flat prisms, melting at  $80^{\circ}$ .

	Found.	Calculated for $C_{14}H_{14}N_2$ .
C	80.15	80.00
H	6.72	6.66

*Action of hydroxyl-amine on methyl-iso-formanilide*.—On adding methyl-iso-formanilide to an aqueous-alcoholic solution of hydroxyl-amine hydrochlorate, a white solid body separates at once. This substance dissolved in dilute alcohol gave on the addition of ammonia a precipitate consisting of small white scales which fused at  $130^{\circ}$ – $131^{\circ}$ . From the method of formation the compound is probably phenyl-methenyl-oxamidine of the structure  $C_6H_5N=C\begin{smallmatrix} H \\ \text{NH.OH} \end{smallmatrix}$ . A combustion gave results agreeing with this formula.

	Found.	Calculated for $C_7H_8N_2O$ .
C	61.71	61.76
H	6.17	5.88

*Formation of di-ortho-tolyl-urea*.—On distilling dry silver form-ortho-toluide, and recrystallising the distillate from absolute alcohol, the urea fusing at  $247^{\circ}$  was obtained.

	Found.	Calculated.
C	74.87	75.00
H	6.68	6.67

Contributions from the Sheffield Biological Laboratory of Yale University.

## A STUDY OF THE PROTEIDS OF THE CORN OR MAIZE KERNEL.

By R. H. CHITTENDEN, Ph. D., *Professor of Physiological Chemistry in Yale University*, and THOMAS B. OSBORNE, Ph. D., *Chemist at the Connecticut Agricultural Experiment Station.*

(Continued from p. 468.)

Another and more successful separation of the globulin into its possible constituents was made by means of fractional heat-coagulation. Obviously, the products so obtained, or at least a portion of them, are coagulated by the process; but if the substance is composed simply of a single body, the several products or coagulums might naturally be expected to have the same composition.

In this experiment, 10 grams of globulin B were dissolved in 10-per cent. salt solution, filtered, the clear fluid heated to 50° in a roomy water-bath and a slight excess of very dilute hydrochloric acid added, by which a copious precipitate was obtained, doubtless an acid compound, leaving the fluid perfectly neutral. This precipitate was washed with salt solution, water, alcohol and ether, and weighed, air-dry, 1 gram (Preparation B<sup>1</sup>).

The perfectly neutral filtrate, on being heated further, became turbid at 57°, with formation of flocks at 66°. The temperature, however, was raised to 70°, where it was held some time, and the precipitate finally filtered off and washed with salt solution, water, alcohol and ether. It weighed, air-dry, about 1 gram (Preparation B<sup>2</sup>). The filtrate became turbid again at 72°, and at 75° a flocculent precipitate made its appearance, which was finally filtered off when the temperature reached 81°. This was treated like the preceding products, and when air-dry weighed 1 gram (Preparation B<sup>3</sup>).

The clear filtrate from this latter coagulum was dialysed free from chlorides, when there resulted a separation of a globulin-like substance, which, after washing with water, alcohol and ether, weighed, air-dry, 1.43 grams (Preparation B<sup>4</sup>).

These several products, on being dried at 110° C. until of constant weight, gave on analysis the following results:

*Analysis of the HCl Precipitate at 50° (B<sup>1</sup>).*

I. 0.3539 gram substance gave 48.7 cc. N at 2.5° C. and 767.8 mm. pressure = 17.33 per cent. N.

II. 0.4731 gram substance gave 0.0016 gram ash = 0.34 per cent.

Percentage of nitrogen in ash-free substance = 17.39.

*Analysis of the Coagulum at 66°-70° (B<sup>2</sup>).*

I. 0.3687 gram substance gave 47.3 cc. N at 2.5° C. and 767.8 mm. pressure = 16.15 per cent. N.

II. 0.3855 gram substance gave 0.0017 gram ash = 0.44 per cent.

Percentage of nitrogen in the ash-free substance = 16.21.

*Analysis of the Coagulum at 75°-81° (B<sup>3</sup>).*

I. 0.3361 gram substance gave 44.9 cc. N at 2.5° C. and 766.1 mm. pressure = 16.78 per cent. N.

II. 0.2015 gram substance gave 0.0004 gram ash = 0.19 per cent.

Percentage of nitrogen in the ash-free substance = 16.81.

*Analysis of the Globulin separated by Dialysis (B<sup>4</sup>).*

I. 0.2993 gram substance gave 0.1810 gram H<sub>2</sub>O = 6.72 per cent. H, and 0.5674 gram CO<sub>2</sub> = 51.72 per cent. C.

II. 0.2595 gram substance gave 0.1596 gram H<sub>2</sub>O = 6.83 per cent. H, and 0.4910 gram CO<sub>2</sub> = 51.60 per cent. C.

III. 0.3300 gram substance gave 47.9 cc. N at 2.5° C. and 762.2 mm. pressure = 18.14 per cent. N.

IV. 0.3265 gram substance gave 0.0016 gram ash = 0.49 per cent.

*Percentage Composition of the Ash-free Substance.*

				Average.
C	51.97	51.85	..	51.91
H	6.75	6.86	..	6.81
N	..	..	18.22	18.22
S	..	..	.. }	23.06
O	..	..	.. }	
				<hr/> 100.00

A comparison of these results shows plainly that the globulin separable from corn meal by the process previously described, as in Preparation B, is composed of at least two dissimilar proteids, or, less probably, is broken into such bodies by the process of heat-coagulation. The products coagulable below 80° are characterised by a comparatively low percentage of nitrogen, while the product (B<sup>4</sup>) separated by dialysis of the filtrate from the coagulum at 80° has a higher content of nitrogen than the original

globulin, resembling in this respect Preparation A<sup>2</sup>, the more insoluble portion of globulin A<sup>1</sup>. This relationship in chemical composition is clearly seen from the following table :

	Globulin B.	Prep. B <sup>1</sup> .*	Prep. B <sup>2</sup> .	Prep. B <sup>3</sup> .	Prep. B <sup>4</sup> .	Prep. A <sup>2</sup> .
C	51.82	..	..	..	51.94	51.76
H	6.85	..	..	..	6.81	6.80
N	17.82	17.39	16.21	16.81	18.22	18.16
S } O }	23.51	..	..	..	23.06	23.28

\* In considering these results it must be remembered that Preparation B<sup>1</sup> is probably nothing more than an acid compound of the mixed globulins.

This close relationship in composition between the products A<sup>2</sup> and B<sup>1</sup> is strongly suggestive of their being the same body, viz., a form of phyto-vitellin especially characterised by non-coagulation below 80° and by very incomplete coagulation above that temperature, even when its solution in sodium chloride is heated to 100°.

Another point to be noted in the above experiment is, that of the 10 grams of globulin (B) started with, only 4.43 grams were recovered in the form of the products B<sup>1</sup> — B<sup>4</sup>, just described. Naturally some loss must have occurred, especially through possible incomplete separation during dialysis of the final solution, but evaporation of the salt-free fluid from which globulin B<sup>4</sup> had separated revealed the presence of about 1.5 grams of non-coagulable matter, either derived from, or present in, the original globulin. The substance so obtained gave a red color with cupric sulphate and potassium hydroxide, the usual proteid reactions with Millon's reagent, no reaction with acetic acid, but a heavy precipitate with acetic acid and potassium ferrocyanide. Addition of acetic acid to a 10-per cent. salt solution of the substance gave a heavy precipitate, possibly in part of globulin, which was still further increased by saturation of the acid fluid with salt. Saturation of a neutral solution of the substance with salt gave no precipitate whatever. Nitric acid produced a distinct turbidity, and addition of an equal volume of alcohol yielded a heavy precipitate.

From this it is plainly evident that in the separation or breaking apart of the original globulin by heat-coagulation there is formed in small quantity a body, or bodies, non-coagulable by heat and readily soluble in water ; in other words, bodies resembling proteoses. That such soluble substances were not present in the



original globulin was proved by boiling a small portion of globulin B in water and then filtering the hot solution. The filtrate gave no reaction whatever for proteids with the biuret test. In other words, the original globulin contained no proteose-like substances, but when dissolved in salt solution and subjected to heat-coagulation such bodies were apparently formed. This was demonstrated in several ways, among others as follows: A portion of globulin B was suspended in water, and the emulsion quickly poured into a 10-per cent. salt solution heated to 75° C. A nearly complete solution resulted, the temperature not falling below 65°. The temperature was immediately raised to 100° and the boiling continued for some minutes, thus killing any possible ferment present, after which the coagulum was filtered off. The somewhat turbid filtrate was evaporated to dryness on a water-bath, a little coagulum forming during the process, and the residue taken up in water. Addition of acetic acid to the strong salt solution produced a heavy precipitate of the vitellin-like proteid, but there still remained in solution some non-precipitable proteid, giving a distinct pink color with the biuret test. While, then, this so-called corn globulin can be approximately separated by heat-coagulation into two dissimilar globulins, there is apparently formed at the same time, presumably by hydrolysis of the less resistant globulin, a small amount of proteose-like bodies, the quantity of which appears to be dependent in part upon the duration of the heating.

The vitellin with 18 or more per cent. of nitrogen is especially characterised, as already indicated, by its pronounced insolubility in weak salt solutions, especially when cold. It is likewise more prone to separate in the spheroidal state. By making use of these facts we were able to separate it directly from the mixed globulin without recourse to coagulation. The method was as follows: 8 grams of globulin B were dissolved in 300 cc. of 5-per cent. salt solution, and the fluid filtered. The clear solution was then diluted with distilled water to about 2 litres, whereby a heavy precipitate resulted. On warming to about 45° C., however, a nearly clear solution was obtained, which on gradual cooling to 8° C. deposited at the end of 48 hours a precipitate of spheroids. This precipitate was then filtered off, dissolved in as little salt solution as possible (warmed to 50° C.), and diluted with distilled water at the same temperature, until a permanent turbidity began to make its appearance. The globulin which separated from this solution on cool-

ing, was wholly soluble in the salt fluid when warmed to 50° C. As the amount of globulin which separated by this treatment was small, the entire mixture was further diluted with an equal volume of water and the resulting precipitate collected. It was then partly dissolved in about 2 litres of quite dilute salt solution, the mixture heated to 50°, and 20-per cent. salt solution added until the globulin had entirely dissolved. On cooling this solution very slowly, ultimately near to 0°, a considerable deposit of very large spheroids resulted, which, after being washed with water, alcohol and ether, weighed, air-dry, 1.5 grams. This product (B<sup>5</sup>), on being dried at 110° C. until of constant weight, gave by analysis the following results:

*Analysis of the Globulin B<sup>5</sup>.*

I. 0.4311 gram substance gave 0.2658 gram H<sub>2</sub>O = 6.85 per cent. H, and 0.8227 gram CO<sub>2</sub> = 52.05 per cent. C.

II. 0.3338 gram substance gave 49 cc. N at 3° C. and 754.2 mm. pressure = 18.10 per cent N.

III. 0.4458 gram substance gave 0.0019 gram ash = 0.42 per cent.

*Percentage Composition of the Ash-free Substance.*

			B <sup>5</sup> .	B <sup>4</sup> .	A <sup>2</sup> .	Globulin B.
C	52.26	..	52.26	51.94	51.76	51.82
H	6.88	..	6.88	6.81	6.80	6.85
N	..	18.17	18.17	18.22	18.16	17.82
S	..	..	22.69	23.06	23.28	0.86
O	..	..				22.65
			<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Comparison of the analysis of this product with that of the original mixed globulin B shows that the nitrogen has been raised to correspond with the percentage in the preceding preparations of vitellin, notably B<sup>4</sup> and A<sup>2</sup>, while the carbon is a trifle higher than in the latter products. Evidently, then, this simple process is sufficient to separate the vitellin from the mixed globulin; the more soluble globulin, with its lower content of nitrogen, remaining in the several solutions.

It is thus evident that the corn or maize globulin originally referred to by Weyl is a mixed substance, composed of at least two dissimilar globulins, one of which approximates in composition to phyto-myosin, the other to phyto-vitellin, although both bodies possess peculiarities of reaction not exactly in accord with the reactions of these two substances as usually described.

d. *Extraction of corn meal with water, and separation of the globulin by ammonium sulphate and dialysis.*

When corn meal is extracted with water there results a solution rich in salts, especially phosphates of the alkalies, in which more or less globulin is dissolved. Direct dialysis of such a solution is followed by separation of the dissolved globulin. It can likewise be precipitated, together with the other proteids present, by saturation of the solution with ammonium sulphate. A concentrated solution, obtained by extracting corn meal with water, when heated grows turbid at about 50° C. (the exact point depending on the concentration of the fluid), with formation of a flocculent coagulum at about 60°. At 64° the solution again becomes turbid, with formation of a second flocculent coagulum at 75°.

The globulin was separated as follows: 6.5 kilos. of corn meal were treated with 10 litres of water, with more or less stirring, for some hours, and the residue of meal re-extracted in the same manner. The united solutions, filtered clear, were saturated with ammonium sulphate. The precipitate so obtained was dissolved as far as possible in water and in 10-per cent. salt solution, leaving quite an insoluble residue. The united aqueous and salt solutions, after filtration, were dialysed until the greater portion of the salt was removed, when there resulted a decided separation of globulin. This globulin was far more insoluble in 10-per cent. solution of sodium chloride than any previous product. In other words, a much larger proportion of this originally soluble globulin passed into an insoluble modification during the process of dialysis, etc., than any product previously separated. That portion still soluble in 10-per cent. salt solution coagulated as follows: turbid at 54°–60°, with formation of flocks at 67°–71°. A second turbidity appeared in the filtered fluid at 69°–72°, but this was very slight, and was not much increased even when the solution was boiled. Addition of acetic acid, however, gave a distinct precipitate. On dialysis of the sodium-chloride solution, the dissolved globulin was deposited. It amounted to only 0.3 gram when air-dry (Preparation F). Dried at 110° C., it yielded by analysis 16.80 per cent. of nitrogen, thus agreeing approximately both in content of nitrogen and in coagulation-point with that portion of the mixed globulin B coagulable below 80°, viz., B<sup>2</sup> and B<sup>3</sup>.

0.2593 gram substance gave 35.2 cc. N. at 2.5° C. and 754.9 mm. pressure = 16.80 per cent. N.

There was not enough substance for an ash determination.

A larger quantity of this globulin, sufficient for a more complete analysis, was obtained from another portion of the corn meal as follows: 5 kilos. of freshly ground corn were thoroughly extracted with water, and the filtered solution precipitated by the addition of ammonium sulphate to saturation. This precipitate was treated with water, and the globulin soluble in the dilute ammonium sulphate solution formed was, after filtration, separated from the fluid by dialysis. After washing the separated globulin with water, alcohol and ether, it weighed, air-dry, 2 grams (Preparation G<sup>1</sup>).

Dried at 110° C. it gave on analysis the following results:

*Analysis of Corn Globulin, Preparation G<sup>1</sup>.*

I. 0.1973 gram substance gave 0.1243 gram H<sub>2</sub>O = 6.99 per cent. H, and 0.3784 gram CO<sub>2</sub> = 52.30 per cent. C.

II. 0.3343 gram substance gave 0.2071 gram H<sub>2</sub>O = 6.88 per cent. H, and 0.6392 gram CO<sub>2</sub> = 52.14 per cent. C.

III. 0.3594 gram substance gave 50.5 cc. N at 17.1° C. and 758.5 mm. pressure = 16.57 per cent. N.

IV. 0.4590 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0433 gram BaSO<sub>4</sub> = 1.28 per cent. S.

V. 0.3159 gram substance gave 0.0025 gram ash = 0.79 per cent.

*Percentage Composition of the Ash-free Substance.*

					Average.
C	52.71	52.56	..	..	52.64
H	7.04	6.94	..	..	6.99
N	..	..	16.70	..	16.70
S	..	..	..	1.28	1.28
O	..	..	..	..	22.39
					<hr/> 100.00

A duplicate of this last product was prepared from another portion of corn meal (5 kilos.) in essentially the same manner. The meal was thoroughly extracted with water, the filtered extract precipitated by saturation with ammonium sulphate, the precipitated proteids filtered off and soaked in water, by which the globulin and some other substances were dissolved. From this dilute ammonium sulphate solution the globulin was separated by dialysis of the salt, and after being washed with water, alcohol and ether, weighed, when air-dry, 2 grams (Preparation H<sup>1</sup>).

Dried at 110° C. and analysed, it yielded the following results:

*Analysis of Corn Globulin, Preparation H<sup>1</sup>.*

I. 0.2825 gram substance gave 0.1769 gram H<sub>2</sub>O = 6.96 per cent. H, and 0.5425 gram CO<sub>2</sub> = 52.37 per cent. C.

II. 0.1553 gram substance gave 0.0989 gram H<sub>2</sub>O = 7.07 per cent. H, and 0.2987 gram CO<sub>2</sub> = 52.45 per cent. C.

III. 0.4200 gram substance gave 59.0 cc. N at 17.2° C. and 765.1 mm. pressure = 16.71 per cent. N.

IV. 0.3118 gram substance gave 0.0021 gram ash = 0.67 per cent. (ash mainly oxide of iron).

V. 0.5500 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0530 gram BaSO<sub>4</sub> = 1.32 per cent. S.

*Percentage Composition of the Ash-free Substance.*

					Average.
C	52.72	52.80	..	..	52.76
H	7.00	7.11	..	..	7.05
N	..	..	16.82	..	16.82
S	..	..	..	1.32	1.32
O	..	..	..	..	22.05
					<hr/>
					100.00

From this description it is obvious that only a portion of the globulins contained in the corn-kernel can be withdrawn by water; in other words, the dilute salt solution which results when corn meal is extracted with water is capable of dissolving only a portion of the globulins present. More important, however, is the fact that the globulin which is so dissolved represents simply that portion of the mixed globulins, previously described, coagulating under 80°, or, to be more exact, it is apparently a body coagulating completely at 75° C. and with a content of nitrogen approximating 16.8 per cent. Furthermore, it is a globulin excessively prone to become insoluble in salt solution by long contact with water or with strong solutions of salt. In other words, it agrees closely with the general descriptions of vegetable myosin except in its peculiar coagulation-points. This view is still further substantiated by the almost complete agreement in composition with animal myosin. This relationship in chemical composition can be clearly seen from the following table:

	Corn myosin. F <sup>1</sup> .	Corn myosin. G <sup>1</sup> .	Corn myosin. H <sup>1</sup> .	Coagulum at 75° from mixed globulin. B <sup>2</sup> .	Animal myosin.*
C	..	52.64	52.72	..	52.82
H	..	6.99	7.05	..	7.11
N	16.80	16.70	16.82	16.81	16.77
S	..	1.28	1.32	..	1.27
O	..	22.39	22.05	..	21.90

\* Average of the analyses of 13 different preparations of animal myosin from various sources. See Studies from Laboratory of Physiological Chemistry, Yale University, 3, 133.



Hence, by this method of extracting corn meal directly with water, and by the use of the method of separation already described, only one globulin is obtained, with a coagulation-point of about  $70^{\circ}$  and agreeing substantially in other respects with the general properties of vegetable myosin. Doubtless the trace of a coagulum obtained at higher temperatures and on the addition of acid is due to a slight admixture of the vitellin-like body. The above statement being correct, it is obvious that the residue of corn meal remaining after complete extraction with water should yield to 10-per cent. salt solution a globulin with 18 per cent. or more of nitrogen unmixed with myosin, providing the latter body has been completely withdrawn from the tissue of the seed. ✓

e. *Extraction of corn meal with 10-per cent. solution of sodium chloride, after previous extraction with water, and separation of the globulin by direct dialysis, and by precipitation with ammonium sulphate and dialysis.*

Extraction of corn meal with 10-per cent. salt solution, after previous extraction with water, yields a solution containing considerable globulin, which can be separated in part by addition of water and completely, or nearly so, on dialysis.

6.5 kilos. of corn meal, after thorough extraction with water (Extract F), were treated several times with an abundance of 10-per cent. salt solution, and the dissolved proteids precipitated from the filtered extract by saturation with pure ammonium sulphate. The precipitate was dissolved, so far as possible, in water and 10-per cent. salt solution, and the united fluids dialysed in running water until the bulk of the salt was removed. The globulin separated in this manner dissolved only partially in 10-per cent. salt solution. The soluble matter coagulated as follows: *slight turbidity at  $60^{\circ}$ – $63^{\circ}$ , with separation of a few flocks at  $71^{\circ}$ – $72^{\circ}$ .* The filtrate from this coagulum grew turbid again at  $81^{\circ}$ – $82^{\circ}$ , flocking at  $91^{\circ}$ – $95^{\circ}$ . Addition of acetic acid to this filtrate gave quite an abundant precipitate. This globulin dissolved by the 10-per cent. salt solution was again separated from the fluid by dialysis. The precipitate so obtained, when washed with water, alcohol and ether, weighed, air-dry, 4.12 grams (Preparation F<sup>2</sup>). It was almost entirely soluble in 10-per cent. salt solution, and when subjected to heat-coagulation yielded only a slight turbidity at  $63^{\circ}$ , with separation of a few flocks at  $73^{\circ}$ . On heating this filtrate nothing further appeared other than a trifling

turbidity, even when the solution was boiled. Addition of acetic acid, however, gave a heavy precipitate. Evidently, therefore, this body is characterised especially by non-coagulation by heat, in a neutral solution, the trifling coagulum observed being unquestionably due to a trace of myosin.

Dried at  $110^{\circ}$  C. until of constant weight, and analysed, the following results were obtained:

*Analysis of Corn Globulin, Preparation F<sup>2</sup>.*

I. 0.3781 gram substance gave 0.2295 gram  $H_2O$  = 6.74 per cent. H, and 0.7205 gram  $CO_2$  = 51.96 per cent. C.

II. 0.3293 gram substance gave 0.2031 gram  $H_2O$  = 6.85 per cent. H, and 0.6253 gram  $CO_2$  = 51.79 per cent. C.

III. 0.3401 gram substance gave 48.8 cc. N at  $3^{\circ}$  C. and 766.9 mm. pressure = 17.99 per cent. N.

IV. 0.3972 gram substance gave 57 cc. N at  $3^{\circ}$  C. and 756.6 mm. pressure = 17.96 per cent. N.

V. 0.7561 gram substance fused with  $KOH + KNO_3$  gave 0.0337 gram  $BaSO_4$  = 0.61 per cent. S.

VI. 0.8611 gram substance fused with  $KOH + KNO_3$  gave 0.0446 gram  $BaSO_4$  = 0.71 per cent. S.

VII. 0.3951 gram substance gave 0.0009 gram ash = 0.22 per cent.

*Percentage Composition of the Ash-free Substance.*

							Average.
C	52.07	51.90	..	..	..	..	51.99
H	6.75	6.86	..	..	..	..	6.81
N	..	..	18.03	18.00	..	..	18.02
S	..	..	..	..	0.61	0.71	0.66
O	..	..	..	..	..	..	22.52
							<hr/> 100.00

The character of this product was verified by another preparation as follows:

5 kilos. of finely ground corn, after being thoroughly extracted with water (Preparation G), were treated with an abundance of 10-per cent. salt solution, and the filtered extract directly dialysed until the salt was entirely removed. The precipitate which separated was washed with water, then redissolved in 10-per cent. salt solution, filtered from the insoluble residue, and again dialysed until the globulin had completely separated once more. This final product was very soluble in salt solutions, and weighed, after being washed with alcohol and ether, 5 grams (Preparation G<sup>2</sup>).

A portion dried at 110° C. gave on analysis the following results:

*Analysis of Corn Globulin, Preparation G<sup>2</sup>.*

I. 0.3063 gram substance gave 0.1857 gram H<sub>2</sub>O = 6.73 per cent. H, and 0.5607 gram CO<sub>2</sub> = 49.91 per cent. C.

II. 0.3205 gram substance gave 0.1925 gram H<sub>2</sub>O = 6.76 per cent. H, and 0.5882 gram CO<sub>2</sub> = 50.04 per cent. C.

III. 0.4245 gram substance gave 63.3 cc. N at 17.0° C. and 764.5 mm. pressure = 17.73 per cent. N.

IV. 0.5045 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0355 gram BaSO<sub>4</sub> = 0.96 per cent. S.

V. 0.4490 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0315 gram BaSO<sub>4</sub> = 0.96 per cent. S.

VI. 0.5435 gram substance gave 0.0125 gram ash = 2.30 per cent.

VII. 0.2865 gram substance gave 0.0662 gram ash = 2.16 per cent.

*Percentage Composition of the Ash-free Substance.*

						Average.
C	51.04	51.17	..	..	..	51.10
H	6.88	6.91	..	..	..	6.90
N	..	..	18.13	..	..	18.13
S	..	..	..	0.98	0.98	0.98
O	..	..	..	..	..	22.89
						<hr/> 100.00

A third preparation of the same order was made as follows: 5 kilos. of corn meal, after extraction with water (Preparation H), were treated with 10-per cent. salt solution, and the filtered extract directly dialysed until the salt was removed. The separated proteid was then filtered off, dissolved again in 10-per cent. salt solution, the solution filtered, and once more dialysed until the proteid had completely separated. The globulin so obtained (Preparation H<sup>2</sup>), after being washed with alcohol and ether, weighed 5 grams, and on analysis (dried at 110° C.) gave the following results:

*Analysis of Corn Globulin, Preparation H<sup>2</sup>.*

I. 0.2844 gram substance gave 0.1728 gram H<sub>2</sub>O = 6.75 per cent. H, and 0.5196 gram CO<sub>2</sub> = 49.82 per cent. C.

II. 0.4564 gram substance gave 0.2699 gram H<sub>2</sub>O = 6.57 per cent. H, and 0.8283 gram CO<sub>2</sub> = 49.49 per cent. C.

III. 0.3892 gram substance gave 57.4 cc. N at 16.3° C. and 759.8 mm. pressure = 17.47 per cent. N.

IV. 0.3767 gram substance gave 56.1 cc. N at 17.4° C. and 755.0 mm. pressure = 17.47 per cent. N.

V. 0.5075 gram substance gave 0.0156 gram ash = 3.07 per cent.

VI. 0.5323 gram substance gave 0.0162 gram ash = 3.04 per cent.

VII. 0.5050 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0338 gram BaSO<sub>4</sub> = 0.92 per cent. S.

VIII. 0.5315 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0345 gram BaSO<sub>4</sub> = 0.89 per cent. S.

*Percentage Composition of the Ash-free Substance.*

							Average.
C	51.38	51.04	..	..	..	..	51.21
H	6.96	6.78	..	..	..	..	6.87
N	..	..	18.02	18.02	..	..	18.02
S	..	..	..	..	0.94	0.91	0.93
O	..	..	..	..	..	..	22.97
							100.00

✓ It is evident from these results that by this process of extraction, first with water and lastly with salt solution, a good separation of the two globulins present in the corn-kernel may be obtained; the myosin-like body passing mainly into the first or aqueous extract, the vitellin dissolving in the 10-per cent. salt solution. When we recall how difficult it many times is to separate closely related proteid bodies, the above method seems fairly successful. In the body last described we have the same globulin (vitellin) which was previously separated from the mixed globulin B, both by heat-coagulation and by what we may term recrystallisation from dilute salt solutions. In their content of nitrogen all of these preparations of vitellin show a close agreement, and, furthermore, a fairly close agreement in carbon. Moreover, the average composition of these products agrees very closely with the generally accepted composition of phyto-vitellin.

The following table shows this relationship very clearly:

	Prep. A <sup>2</sup> .	Prep. B <sup>4</sup> .	Prep. B <sup>5</sup> .	Prep. F <sup>2</sup> .	Prep. G <sup>2</sup> .	Prep. H <sup>2</sup> .	Phyto-vitellin.*
C	51.76	51.94	52.26	51.99	51.10	51.21	51.88
H	6.80	6.81	6.88	6.81	6.90	6.87	7.51
N	18.16	18.22	18.17	18.02	18.13	18.02	18.08
S } O }	23.28 23.06	23.06 22.69	22.69 22.52	0.66 22.52	0.98 22.89	0.93 22.97	0.60 21.93

\* Prepared from pumpkin seeds and analysed by Barbieri by Weyl's method (J. prakt. Chem. 18, 102-116).

As is seen from the table of results, the vitellin is noticeably different from the corn myosin in having a smaller percentage of sulphur, the latter containing on an average 1.27 per cent. of

sulphur, while the vitellin contains only about 0.85 per cent. It is also noticeable that preparations G<sup>2</sup> and H<sup>2</sup> contain a lower percentage of carbon than the other products. What the explanation of this is we cannot say, although it is to be remembered that these two preparations of vitellin (unlike F<sup>2</sup>) were separated from the salt solution by direct dialysis, without previous precipitation with ammonium sulphate, and possibly are not quite so pure.

As to the respective quantities of these two globulins present in the kernel, it would appear that the vitellin is greatly in excess, although it is to be remembered that the myosin is more readily changed into an insoluble modification by the process of separation, and hence considerable loss occurs.

From the foregoing it is plain that the mixed globulin first described, obtained by direct extraction of corn meal with 10-per cent. salt solution, as preparations A-D, is mainly a mixture of two globulins resembling in composition myosin and vitellin, the composition of the mixed product being readily explainable, in the main, on that hypothesis. The coagulation-points of these two globulins, however, are far from according with the coagulation-points of phyto-myosin and vitellin as usually given. What we have chosen to call corn myosin shows a tendency to coagulate at several points, as already described, but is mainly coagulable at about 70°, while the vitellin-like body in a neutral salt solution appears almost non-coagulable by heat. In fact, the latter body partakes in many respects of the character of hetero-albumose, and is perhaps as closely related to this body as to the true globulins. The myosin-like body is evidently much like the peculiar globulin (not analysed) described by Martin<sup>1</sup> as present in papaw juice, the coagulation-temperatures and general reactions of the two bodies being apparently much the same.

There is every indication of gradual changes being produced by the application of heat to the solutions of these globulins, and, in our opinion, the variable coagulation-points observed are an index of this fact. Sidney Martin<sup>2</sup> has shown that the myosin present in the kernels of wheat and rye is transformed into an insoluble body by simple warming of the 10-per cent. sodium-chloride solution of the globulin at 35°-40° C. for some hours, and Vines<sup>3</sup> claims that phyto-vitellin may undergo transformation into myosin. The peculiar heat-coagulation points of the two

<sup>1</sup> *Journal of Physiology* 6, 353.

<sup>2</sup> *Ibid.* 8, "On two classes of vegetable globulins."

<sup>3</sup> *Ibid.* 3, 93-114.



corn globulins may possibly be due in part to rapid conversion into the insoluble or albuminate stage and its separation as a coagulum.

There is, however, evidence of still another globulin in the corn kernel, differing from all of the preceding preparations, but, doubtless, sometimes present in small quantity in the products already described.

*f. A more soluble globulin which separates from its solution only after long-continued dialysis.*

The two most important characteristics of a globulin are its solubility in various strengths of salt solution and its insolubility in water; hence the removal of the salt from a globulin containing solution, by dialysis, constitutes one of the most effectual methods of separating such proteids from their solutions, provided the removal of the salts is complete. Under ordinary circumstances a globulin dissolved in a salt solution separates quite rapidly when the solution is subjected to dialysis. Obviously, the rate of separation will depend greatly upon the endosmotic equivalent of the salts present and the solubility of the globulin, but under most circumstances the separation is practically complete some time before every trace of the salt is removed. Sodium chloride diffuses much more rapidly than ammonium sulphate; indeed, the latter salt requires a very long time for its complete removal, even when dialysed in running water of a fair degree of purity. The same is true of the phosphates of the alkalies present in the corn kernel, so that an extract of corn meal, for example, made with 10-per cent. salt solution, may be dialysed until every trace of chloride is removed and still give a reaction for phosphates.

In the separation of the mixed globulins from the corn kernel as already described, it will be remembered that the usual procedure was to precipitate the filtered salt extract of the meal with ammonium sulphate added to saturation. The precipitated proteids were collected on a filter, allowed to drain, and then dissolved so far as possible in water and 10-per cent. solution of sodium chloride. Obviously, such a solution after filtration when ready for dialysis, would contain, in addition to the proteids, anywhere from 5 to 8 per cent. of sodium chloride, and possibly 1 per cent. of ammonium sulphate. In separating the dissolved globulin by dialysis it was our custom to continue the dialysis until the solution failed to give any reaction for chlorides with silver nitrate and nitric acid, considering that when that point was reached the globulin would be completely precipitated. Thus, in the prepa-

ration of globulin B from 25 kilos. of corn meal, after the method just indicated, the dialysis of the sodium-chloride and ammonium-sulphate solution was continued (in running water) for two weeks, at the end of which time the chloride was entirely removed, and over 42 grams of globulin had separated. The clear filtered fluid still contained a trace of sulphate, and as an experiment it was again exposed to dialysis in small parchment bags suspended in running water, for one week longer. Greatly to our surprise, a second deposit of globulin formed, which, after being washed with water, alcohol and ether, weighed, air-dry, 2.8 grams (Preparation B<sup>6</sup>).

The filtrate from this product was again returned to the dialysers for ten days longer, when a third deposit of globulin formed, which, after being washed and dried, weighed 1.3 grams (Preparation B<sup>7</sup>). The filtrate from this product gave no further deposit even when dialysed in distilled water.

These two preparations were unquestionably true globulins; both were wholly insoluble in water, but dissolved readily in dilute salt solutions. Preparation B<sup>6</sup>, dissolved in 10-per cent. solution of sodium chloride, coagulated as follows: the solution grew slightly turbid at 59° and flocked at 62°. The filtrate from this coagulum grew slightly turbid again at 69°, but there was no separation of flocks, even when the mixture was boiled, or on the addition of acetic acid. Evidently, therefore, the substance was precipitated at 62°. Addition of potassium ferrocyanide to the acid fluid, however, gave a slight precipitate, indicating that the substance was not wholly coagulable by heat, or else that some little proteose-like substance had been formed in the process.

The composition of the globulin, after drying at 110° C. until of constant weight, was as follows:

*Analysis of Corn Globulin, Preparation B<sup>6</sup>.*

I. 0.3094 gram substance gave 0.1915 gram H<sub>2</sub>O = 6.87 per cent. H, and 0.5911 gram CO<sub>2</sub> = 52.10 per cent. C.

II. 0.3516 gram substance gave 0.2121 gram H<sub>2</sub>O = 6.70 per cent. H, and 0.6721 gram CO<sub>2</sub> = 52.13 per cent. C.

III. 0.3895 gram substance gave 47.5 cc. N at 2.5° C. and 756.0 mm. pressure = 15.12 per cent. N.

IV. 0.3798 gram substance gave 46.9 cc. N at 5° C. and 759.4 mm. pressure = 15.22 per cent. N.

V. 0.4427 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0407 gram BaSO<sub>4</sub> = 1.26 per cent. S.

VI. 0.3895 gram substance gave 0.0019 gram ash = 0.50 per cent.

*Percentage Composition of the Ash-free Substance.*

						Average.
C	52.36	52.39	..	..	..	52.38
H	6.90	6.74	..	..	..	6.82
N	..	..	15.20	15.30	..	15.25
S	..	..	..	..	1.26	1.26
O	..	..	..	..	..	24.29
						<hr/> 100.00

Judging from the coagulation-point and composition of this product, it is a globulin distinctly different from the preceding preparations. The above data taken together clearly prove that it is not a mere trace of myosin, vitellin, or both, which had escaped separation, although a trace of these bodies may have been mixed with it, as is indeed suggested by the turbidity at 69°, but that it represents a more soluble globulin than either of the preceding, and one containing a much lower percentage of nitrogen. It resembles myosin rather than vitellin, yet differs from them both in composition, in the temperature at which it coagulates, and in its marked solubility in very dilute solutions of salts other than chlorides.

The low content of nitrogen in this globulin is substantiated by the percentage of nitrogen in the second product (B'), which is undoubtedly the same as the preceding.

*Analysis of Corn Globulin, Preparation B'.*

I. 0.3051 gram substance gave 36.6 cc. N at 3.0° C. and 757.2 mm. pressure = 14.84 per cent. N.

II. 0.3987 gram substance gave 0.0085 gram ash = 2.13 per cent.

Percentage of nitrogen in the ash-free substance = 15.16.

Without doubt, traces of this globulin may be carried down with the other globulins, especially with the myosin and with the mixed globulin, and this may be the cause of the low coagulation-point occasionally observed in the other products. On the other hand, if the preliminary dialysis for the separation of the two more insoluble globulins is not continued sufficiently long, then the product obtained on subsequent dialysis will contain some myosin, and possibly vitellin.

This is well illustrated in the following experiment: The proteids precipitated from a sodium-chloride extract of 5 kilos. of corn meal (Preparation E) by ammonium sulphate, and then dissolved

in water and 10-per cent. salt solution, were dialysed in running water for one week, when a considerable separation of globulin occurred. This was filtered off, and the solution, which contained an appreciable amount of salt, was again dialysed for one week longer, yielding 1.16 grams of air-dry globulin (Preparation E<sup>6</sup>). The filtrate, which contained a trace of sulphate, was again dialysed for one week, when there resulted a small separation of globulin, weighing, air-dry, 0.25 gram (Preparation E<sup>7</sup>). These were dried at 110° C. and analysed with the following results:

*Analysis of the Globulin E<sup>6</sup>.*

I. 0.3728 gram substance gave 48.1 cc. N at 3.0° C. and 768.3 mm. pressure = 16.20 per cent. N.

II. 0.4817 gram substance gave 0.0075 gram ash = 1.56 per cent.

*Analysis of the Globulin E<sup>7</sup>.*

I. 0.1700 gram substance gave 20.6 cc. N at 3.0° C. and 767.7 mm. pressure = 15.21 per cent. N.

Not enough substance for an ash determination.

From this it is sufficiently evident that the first product (E<sup>6</sup>) is, as might be expected, a mixture of corn myosin with the more soluble globulin; while the latter product (E<sup>7</sup>) corresponds closely, at least in its content of nitrogen, with the preceding products of like nature.

A tabular arrangement of the analyses of what we may term pure preparations of this globulin shows a fairly close agreement in composition.

	Prep. B <sup>6</sup> .	Prep. B <sup>7</sup> .	Prep. E <sup>7</sup> .
C	52.38	..	..
H	6.82	..	..
N	15.25	15.16	15.21
S	1.26	..	..
O	24.29	..	..

From the foregoing descriptions this body is to be considered as a third globulin present in small amount in the corn kernel, and characterised especially by a low content of nitrogen, 15.2 per cent., and with a coagulation-point at about 62° C.

*g. Insoluble products derived from the foregoing globulins.*

As is well known, many proteid bodies undergo change by long contact with water or by contact with strong salt solutions, being converted thereby into insoluble modifications resembling albumi-

nates, soluble only in dilute alkaline fluids, or, it may be, by longer action, into bodies closely resembling coagulated proteids. This is notably true of animal myosin, of freshly precipitated syntonin, and of certain vegetable globulins. We have found this likewise true of one or more of the corn globulins just described. Thus, when a perfectly clear sodium-chloride extract of corn meal is dialysed and the globulin thereby precipitated, a portion of the product is changed in the process, as evidenced by its being no longer soluble in solutions of sodium chloride of any strength. This insoluble portion, however, is dissolved by dilute solutions of sodium carbonate, being precipitated therefrom on neutralisation, apparently as alkali-albuminate. Again, in precipitating the proteids from a sodium-chloride extract of corn meal by saturation of the solution with ammonium sulphate, a portion of the globulin precipitated thereby loses its solubility in dilute salt solutions, being plainly converted into the same insoluble modification. Further, if by chance the ammonium sulphate used in the precipitation of the proteids is acid, the transformation is far more rapid and complete, apparently in proportion to the acidity. Naturally, there may likewise occur, in this case, some formation of insoluble acid compounds.

The details of the formation and separation of some of these insoluble transformation products are as follows:

1. *Insoluble products formed by the action of ammonium sulphate on the mixed globulin directly extracted from corn by 10-per cent. salt solution.*

In the preparation of the mixed globulin B, 25 kilos. of finely ground corn were extracted with an abundance of 10-per cent. salt solution at the temperature of the room, and the resultant solution filtered through filter-paper, yielding a perfectly clear fluid. All of the proteids were then precipitated by saturation of the solution at the ordinary temperature with recrystallised and perfectly neutral ammonium sulphate. This precipitate was then treated with a small volume of water, sufficient to make with the adherent salt a 1- to 3-per cent. solution of ammonium sulphate, and then with 10-per cent. solution of sodium chloride as long as the latter exerted any solvent action. As a result there remained quite an amount of insoluble matter, wholly insoluble in water and salt solutions, but readily dissolved by solutions of sodium carbonate of sufficient strength. It was, therefore, treated with a solution of



1-per cent. sodium carbonate, the fairly clear fluid filtered through paper, and the proteid reprecipitated by neutralisation with dilute hydrochloric acid. After being washed with water until free from salts, then with alcohol and ether, it weighed, air-dry, 4.7 grams (Preparation B<sup>x</sup>). In this connection it may be well to recall the fact that in this extraction of corn there were obtained 42 grams of purified mixed globulin and 4.1 grams of the more soluble globulin, thus indicating that approximately one-tenth of the total amount of globulin was converted into this insoluble modification, presumably through the action of the ammonium sulphate. This alteration-product, after being dried at 110° C., gave on analysis the following results :

*Analysis of Preparation B<sup>x</sup>.*

I. 0.4400 gram substance gave 0.2781 gram H<sub>2</sub>O = 7.02 per cent. H, and 0.8657 gram CO<sub>2</sub> = 53.66 per cent. C.

II. 0.3960 gram substance gave 0.2504 gram H<sub>2</sub>O = 7.02 per cent. H, and 0.7769 gram CO<sub>2</sub> = 53.51 per cent. C.

III. 0.3447 gram substance gave 44.1 cc. N at 2.0° C. and 763.2 mm. pressure = 16.02 per cent. N.

IV. 0.7012 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0557 gram BaSO<sub>4</sub> = 1.09 per cent. S.

V. 0.5472 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0476 gram BaSO<sub>4</sub> = 1.19 per cent. S.

VI. 0.5810 gram substance gave 0.0039 gram ash = 0.67 per cent.

*Percentage Composition of the Ash-free Substance.*

						Average.
C	54.02	53.87	..	..	..	53.95
H	7.05	7.05	..	..	..	7.05
N	..	..	16.13	..	..	16.13
S	..	..	..	1.09	1.19	1.14
O	..	..	..	..	..	21.73
						<hr/> 100.00

Two similar preparations, each from 5 kilos. of corn meal, were obtained in much the same manner as the preceding, except that, through the inadvertent use of slightly acid ammonium sulphate in the precipitation of the proteids, a far larger proportion of the globulin was converted into this insoluble modification and, further, in both cases the insoluble product contained considerable matter which would not dissolve even in 1- to 3-per cent. sodium carbonate. That portion soluble in 1-per cent. sodium carbonate

was filtered off and in each case precipitated by neutralisation with dilute hydrochloric acid.

The products were then washed free from salts with water, with alcohol, and thoroughly extracted with ether (Preparations M<sup>x</sup> and N<sup>x</sup>).

On analysis the following results were obtained, which show fairly close agreement with the preceding data:

#### *Analysis of Preparation M<sup>x</sup>.*

I. 0.3874 gram substance gave 0.2403 gram H<sub>2</sub>O = 6.89 per cent. H, and 0.7497 gram CO<sub>2</sub> = 52.77 per cent. C.

II. 0.4460 gram substance gave 0.2749 gram H<sub>2</sub>O = 6.85 per cent. H, and 0.8595 gram CO<sub>2</sub> = 52.57 per cent. C.

III. 0.4373 gram substance gave 55.5 cc. N at 7.3° C. and 765.6 mm. pressure = 15.64 per cent. N.

IV. 0.8302 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0693 gram BaSO<sub>4</sub> = 1.14 per cent. S.

V. 0.6978 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0577 gram BaSO<sub>4</sub> = 1.13 per cent. S.

VI. 0.9290 gram substance gave 0.0176 gram ash = 1.89 per cent.

#### *Percentage Composition of the Ash-free Substance.*

						Average.
C	53.79	53.59	..	..	..	53.69
H	7.02	6.98	..	..	..	7.00
N	..	..	15.94	..	..	15.94
S	..	..	..	1.16	1.15	1.16
O	..	..	..	..	..	22.21
						<hr/> 100.00

#### *Analysis of Preparation N<sup>x</sup>.*

I. 0.3777 gram substance gave 0.2315 gram H<sub>2</sub>O = 6.80 per cent. H, and 0.7174 gram CO<sub>2</sub> = 51.79 per cent. C.

II. 0.3437 gram substance gave 0.2101 gram H<sub>2</sub>O = 6.79 per cent. H, and 0.6502 gram CO<sub>2</sub> = 51.59 per cent. C.

III. 0.4419 gram substance gave 56.6 cc. N at 7.4° C. and 763.6 mm. pressure = 15.74 per cent. N.

IV. 0.7266 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0609 gram BaSO<sub>4</sub> = 1.15 per cent. S.

V. 0.8527 gram substance fused with KOH + KNO<sub>3</sub> gave 0.0634 gram BaSO<sub>4</sub> = 1.02 per cent. S.

VI. 0.7776 gram substance gave 0.0229 gram ash = 2.94 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	53.39	53.19	..	..	..	53.29
H	7.00	6.99	..	..	..	7.00
N	..	..	16.23	..	..	16.23
S	..	..	..	1.18	1.05	1.12
O	..	..	..	..	..	22.36
						<hr/> 100.00

From these three analyses it is plainly manifest that these insoluble products formed in the manner indicated are essentially the same. Their composition, moreover, indicates that in the formation of these bodies a decided alteration occurs, if we assume that they are formed from the mixed globulins already described. In fact, none of the globulins thus far identified could yield products with the high content of carbon noted here without undergoing a change of considerable magnitude. Obviously, we do not know how much of this change in composition results from the action of the ammonium sulphate and how much from the action of the dilute sodium carbonate, but inasmuch as we have obtained from a mixed globulin an insoluble body having the same low content of nitrogen, without the use of the sodium carbonate, it seems fair to presume that the change in composition is independent of any action of the dilute alkaline fluid.

2. *Insoluble products formed by the action of ammonium sulphate on the globulin extracted from corn by water, and on the globulin extracted by 10-per cent. solution of salt after previous extraction of the corn with water.*

In the preparation of extract F, 6.5 kilos. of corn meal were treated with cold water—about 14 litres—in two or more portions, and the filtered solutions precipitated with neutral ammonium sulphate added to saturation. This precipitate was then treated with water and 10-per cent. salt solution as long as anything was dissolved.

The residue was then dissolved in 0.5-per cent. solution of sodium carbonate, filtered, and the proteid precipitated by neutralisation. After being washed with water, alcohol and ether, it weighed, air-dry, 1.35 grams (Preparation F<sup>2</sup>).

Analysed, it gave the following results:

*Analysis of Preparation F<sup>2</sup>.*

1. 0.2557 gram substance gave 0.1581 gram H<sub>2</sub>O = 6.86 per cent. H, and 0.4974 gram CO<sub>2</sub> = 53.05 per cent. C.

II. 0.3350 gram substance gave 43.9 cc. N at 3° C. and 759.3 mm. pressure = 16.27 per cent. N.

III. 0.3800 gram substance gave 0.0028 gram ash = 0.73 per cent.

*Percentage Composition of the Ash-free Substance.*

			Average.
C	53.43	..	53.43
H	6.90	..	6.90
N	..	16.39	16.39
O	..	..	23.28
S	..	..	
			100.00

The residue of corn meal remaining after the above extraction with water, was then extracted with 10-per cent. solution of sodium chloride, the filtered solution precipitated with ammonium sulphate, and the proteids treated exactly as described under the aqueous extract. As a result, 1.45 grams of insoluble proteid were obtained, which on analysis gave the following results:

*Analysis of Preparation F<sup>v</sup>.*

I. 0.4967 gram substance gave 0.3086 gram H<sub>2</sub>O = 6.90 per cent. H, and 0.9537 gram CO<sub>2</sub> = 52.36 per cent. C.

II. 0.3520 gram substance gave 45.1 cc. N at 3° C. and 749.1 mm. pressure = 15.69 per cent. N.

III. 0.4165 gram substance gave 0.0049 gram ash = 1.17 per cent.

*Percentage Composition of the Ash-free Substance.*

			Average.
C	52.98	..	52.98
H	6.98	..	6.98
N	..	15.87	15.87
S	..	..	24.17
O	..	..	
			100.00

3. *Insoluble products formed through the action of water on the globulins extracted from corn meal by water and by 10-per cent. salt solution.*

The sodium chloride and ammonium sulphate solutions of the globulins filtered off from the two preceding preparations, F<sup>x</sup> and F<sup>v</sup>, were dialysed in running water until the salts were practically all removed and the globulins separated from their respective solutions.

On attempting to dissolve these products in 10-per cent. solution of sodium chloride, a certain proportion remained insoluble;

in other words, during the long dialysis a portion of each globulin, formerly soluble in the salt solution, had become insoluble. These insoluble products were filtered off, washed thoroughly with 10-per cent. salt solution, dissolved in 1-per cent. sodium carbonate, the solution filtered and neutralised with dilute hydrochloric acid. The precipitated proteids, after being washed with water, alcohol and ether, weighed, air-dry, respectively 1.2 grams (Preparation  $F^{za}$ ) and 1.73 grams (Preparation  $F^{va}$ ), the former having come from the globulin extracted by water alone, and hence presumably formed from the myosin-like globulin, while the latter product,  $F^{va}$ , on similar grounds must have been formed from the vitellin-like globulin or from some adherent body.

These two products, on analysis, gave the following results:

*Analysis of Preparation  $F^{za}$ .*

I. 0.2278 gram substance gave 29.8 cc. N at 2.5° C. and 756.9 mm. pressure = 16.24 per cent. N.

II. 0.3678 gram substance gave 0.0029 gram ash = 0.79 per cent.

Percentage of N in the ash-free substance = 16.37.

*Analysis of Preparation  $F^{va}$ .*

I. 0.2795 gram substance gave 0.1740 gram  $H_2O$  = 6.92 per cent. H, and 0.5302 gram  $CO_2$  = 51.74 per cent. C.

II. 0.2844 gram substance gave 38.3 cc. N at 3.0° C. and 760.3 mm. pressure = 16.74 per cent. N.

III. 0.4025 gram substance gave 0.0018 gram ash = 0.45 per cent.

*Percentage Composition of the Ash-free Substance.*

			Average.
C	51.97	..	51.97
H	6.95	..	6.95
N	..	16.82	16.82
S	..	.. }	24.26
O	..	.. }	
			<hr/> 100.00

Arranging these several results in tabular form, it becomes easy to draw certain general conclusions from the data:

	$Bz.$	$Mz.$	$Nz.$	$Fz.$	$Fv.$	$Fza.$	$Fva.$
C	53.95	53.69	53.29	53.43	52.98	..	51.97
H	7.05	7.00	7.00	6.90	6.98	..	6.95
N	16.13	15.94	16.23	16.39	15.87	16.37	16.82
S	1.14	1.16	1.12 }	23.28	24.17	..	24.26
O	21.73	22.21	22.36 }				



	Myosin-like globulin.	Very soluble globulin, B <sup>8</sup> .	Vitellin-like globulin, F <sup>2</sup> .
C	52.72	52.38	51.99
H	7.05	6.82	6.81
N	16.82	15.25	18.02
S	1.32	1.26	0.66
O	22.05	24.29	22.52

With the exception of the product F<sup>va</sup>, all of these insoluble bodies have the same general composition, and are alike characterised by a high content of carbon. Taking into consideration the percentage of nitrogen in these bodies and the nitrogen of the several globulins present in the corn kernel, it is evident that the vitellin-like globulin cannot well be considered as an antecedent of these insoluble products. These latter bodies are unquestionably formed from the myosin-like globulin and the still more soluble globulin with 15.25 per cent. of nitrogen. Doubtless it is this greater tendency of these two globulins to pass into insoluble modifications which facilitates the purification of the vitellin-like globulin. Thus the like preparations, F<sup>x</sup> and F<sup>y</sup>, coming as they do from the aqueous extract and from the sodium-chloride extract of the corn respectively, indicate a common origin, and it can be explained only on the supposition (certainly plausible enough) that the myosin-like globulin, not being wholly dissolved by the water extract, is dissolved together with the vitellin by the 10-per cent. salt solution and then later changed into the insoluble modification just described. Again, the content of sulphur is of significance in this connection, in that the myosin-like globulin and its still more soluble neighbor are both characterised by a fairly high content of sulphur, while the vitellin-like globulin contains less than 1 per cent. of this element.

In conclusion, then, we are apparently justified in making the statement that through the long-continued action of water and strong solutions of salt, as ammonium sulphate, the two globulins with a low content of nitrogen are gradually changed into insoluble modifications, which are especially characterised by a relatively high content of carbon.

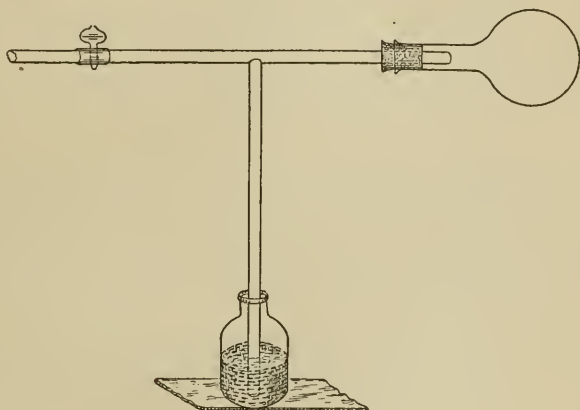
(To be continued.)

5-12-1912

## A SIMPLE FORM OF APPARATUS FOR A COMMON LECTURE EXPERIMENT.

BY W. A. NOYES.

The apparatus usually employed to demonstrate that the volume of sulphur dioxide formed by burning sulphur equals the volume of oxygen consumed, is expensive and somewhat difficult to manage. I have found that the simple arrangement illustrated below answers excellently for the purpose.

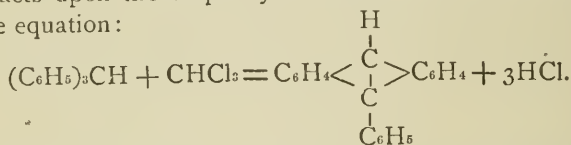


In the flask, having a capacity of 250 to 300 cc., is placed a small piece of sulphur. The flask is then filled with oxygen by displacement of the air. The rubber stopper on the end of the T-tube is then inserted, and by means of the water air-pump the flask is exhausted till the mercury rises to a height of about 300 mm. in the lower arm of the tube. After closing the stop-cock and placing a mark at the top of the mercury in the tube, the sulphur is ignited by heating the flask with a small flame. The combustion takes place quietly, and when it is completed, the flask, being thin, cools quickly to its original temperature. When cold the mercury will stand very nearly at the same level as before the combustion, usually a very little higher.

# THE REACTION BETWEEN TRI-PHENYL-METHANE AND CHLOROFORM IN THE PRESENCE OF ALUMINIUM CHLORIDE.

BY C. E. LINEBARGER.

Messrs. Friedel and Crafts,<sup>1</sup> in investigating the reaction of chloroform on benzene in the presence of aluminium chloride, found that phenyl-anthracene was formed as a secondary product. The most probable explanation of its formation is that the chloroform reacts upon the tri-phenyl-methane formed in accordance with the equation:



On the suggestion of M. Friedel, I took up the investigation of the subject, and have found that chloroform really does act upon tri-phenyl-methane in the presence of aluminium chloride, giving as principal product phenyl-anthracene. After numerous experiments, I found that the following way of conducting the reaction gave the best yield. In no case, however, was a very good yield obtained; the best being about 15 per cent. of the theoretical. Also the amount of phenyl-anthracene obtained was not at all uniform, experiments carried out under perfectly similar conditions giving quite different results.

To a solution of 50 grams pure tri-phenyl-methane in 600 grams anhydrous chloroform, 40 grams of aluminium chloride were added in three portions. On the addition of the first portion hydrochloric acid began to pass off slowly, more rapidly on heating to 40°–50°. When all the aluminium chloride had been added, I heated to gentle boiling for a few minutes. I found it not advisable to boil longer than was necessary to cause a little less than the theoretical quantity (calculated according to above equation) to pass off. The contents of the flask were now treated first with cold, then with boiling water. The chloroform solution when drawn off was distilled and the residue dissolved in a little benzene. On adding a relatively large quantity of petroleum ether, a resinous precipitate was thrown down, which was filtered off. I

<sup>1</sup> Ann. chim. phys. (6) 1, 495.

distilled off the mixture of benzene and petroleum from the filtrate and crystallised the residue from alcohol. By two crystallisations almost white tablets of phenyl-anthracene were obtained.

In regard to the properties of the phenyl-anthracene obtained in this way, I found them to agree entirely with those found by other investigators. A melting-point determination carefully made with a good thermometer divided in tenths of a degree, gave  $152.8^{\circ}$ .

An analysis gave

	Calculated for $C_{20}H_{14}$ .	Found.
C	94.48	94.57
H	5.52	5.49

From the alcoholic mother-liquors I succeeded in isolating a substance crystallising well, and melting at  $87^{\circ}$ – $88^{\circ}$ . v. Baeyer<sup>1</sup> mentions, as one of the products of reduction of phenyl-oxanthranol, a substance melting at  $86^{\circ}$ – $88^{\circ}$ , which he takes to be a mixture of di- and tetra-hydrides of phenyl-anthracene. I did not obtain enough of the substance in question to make an exhaustive study, it being formed in minute quantities only; but from the analysis I conclude that it is a hydride of phenyl-anthracene. The results of the analysis would seem to show that it was the di-hydride, and it would be possible for a reduction to take place in the reaction. Nevertheless it is difficult to conceive how the reduction could give the tetra-hydride.

The analyses gave

	Calculated for $C_{20}H_{16}$ .	Calculated for $C_{20}H_{18}$ .	I. Found.	II.
C	93.78	93.03	93.64	93.7
H	6.22	6.97	6.35	6.49

The formation of phenyl-anthracene by the action of tri-phenyl-methane upon chloroform in the presence of aluminium chloride, throws some light upon the mechanism of the reaction between benzene and chloroform in the presence of aluminium chloride. At a certain stage of the reaction the chloroform begins to act upon the newly formed tri-phenyl-methane to form phenyl-anthracene and other products. Thus a certain portion of tri-phenyl-methane is destroyed and the yield is less. On this score an objection might be raised against the methods in which the reaction is prolonged for a long time. It is true, hydrochloric acid passes off all the time, but it is not entirely due to the

<sup>1</sup>Ann. Chem. (Liebig) **202**, 62.

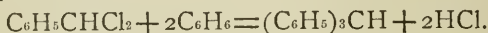
action of chloroform on benzene. The tri-phenyl-methane is also acted upon by the chloroform. What renders this more plausible is, that in the method of Friedel and Crafts, where the reaction is only continued for a few hours, a better yield is obtained than by any other method.

CLARK UNIVERSITY, WORCESTER, MASS.

## THE ACTION OF BENZENE ON BENZAL CHLORIDE IN THE PRESENCE OF ALUMINIUM CHLORIDE.

BY C. E. LINEBARGER.

Nearly all the text-books on organic chemistry state that tri-phenyl-methane is formed by the action of benzal chloride on benzene in the presence of aluminium chloride, in accordance with the equation:



The only recorded experimental proof of this assertion, as far as my knowledge goes, is in a foot-note by Böttiger,<sup>1</sup> who remarks that small quantities of tri-phenyl-methane are formed if benzal chloride and benzene be warmed together with a little zinc dust. I have made a more detailed examination of this reaction, in the hope of obtaining, not only tri-phenyl-methane, but also a dihydride of di-phenyl-anthracene. That a dihydride of di-phenyl-anthracene would be formed in a reaction of this kind seemed probable, as Anschütz,<sup>2</sup> by the reaction of ethylidene bromide on benzene in presence of aluminium chloride, obtained the dihydride of di-methyl-anthracene.

It appeared to make no difference in the yield whether the benzal chloride was run into the benzene containing the chloride of aluminium, or the aluminium chloride added to the mixture of benzene and benzal chloride.

One noteworthy feature of the reaction was the small amount of aluminium chloride required. After several trials with different proportions of the ingredients, I decided upon the following method of conducting the reaction: I added 25 grams aluminium

<sup>1</sup> Ber. d. chem. Ges. 12, 976.

<sup>2</sup> Ann. Chem. (Liebig) 235, 305.



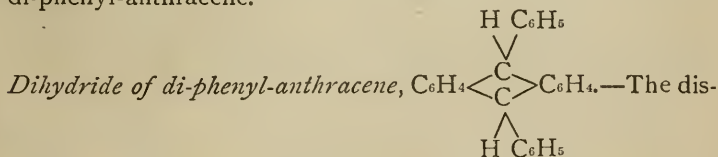
chloride to a mixture of 200 grams benzal chloride (b. p.  $206^{\circ}$ – $207^{\circ}$ ) and 1000 grams benzene, and gently heated on the water-bath. At about  $40^{\circ}$ – $50^{\circ}$  the reaction begins, and at  $50^{\circ}$ – $60^{\circ}$  takes place quite rapidly. When nearly the theoretical quantity of hydrochloric acid has passed off, which occurs in about two hours, the contents of the flask are heated to boiling for a few minutes. When cool, the product of the reaction is treated with water. After drawing off the water from the benzene solution, I distilled off the latter and subjected the residue to fractional distillation.

Almost nothing passed over below  $260^{\circ}$ ; at this point a decomposition of higher-chlorinated products took place with evolution of acid fumes. Between  $300^{\circ}$ – $360^{\circ}$  the larger portions passed over and the distillate solidified in the receiver. Another small distillate was collected between  $360^{\circ}$ – $420^{\circ}$ , and also one between  $420^{\circ}$  and red heat.

The fraction between  $300^{\circ}$ – $360^{\circ}$  dissolved readily in hot benzene, from which on cooling the characteristic crystals of the compound of benzene and tri-phenyl-methane were deposited. By crystallisation from alcohol, pure tri-phenyl-methane was obtained. With 200 grams benzal chloride I obtained on an average about 80–90 grams pure tri-phenyl-methane, or about 30 per cent. of the theoretical yield. If the benzal chloride be pure, but traces of di-phenyl-methane are formed. The method is certainly excellent for obtaining tri-phenyl-methane as regards cheapness, rapidity of execution and yield.

The properties of tri-phenyl-methane, prepared by this reaction, are exactly those described by other investigators. I made determinations of both melting- and boiling-point. The melting-point, taken with a corrected thermometer divided in tenths of a degree, was  $93.4^{\circ}$ . The boiling-point, taken with a Baudin corrected thermometer, was  $357^{\circ}$  under 758 mm.

From the higher-boiling distillates I obtained a hydrocarbon with the composition  $C_{26}H_{20}$ , which is without doubt the dihydride of di-phenyl-anthracene.



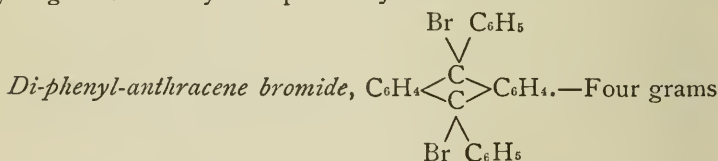
tillates boiling above  $400^{\circ}$  were redistilled under a pressure of

about 25 mm. At 200° a light-yellow liquid passed over which solidified in the receiver; this proved to be tri-phenyl-methane. At 250° I changed the receiver and collected a small distillate between 250°–300°. I now removed the thermometer, changed the receiver, and heated as long as anything distilled. The dark-red viscous distillate thus obtained was dissolved in a hot mixture of alcohol and benzene. After standing some time, a dark-red oil separated out. The clear solution was decanted from this oil, and it gave by slow evaporation a crop of microscopic crystals. By two crystallisations from boiling benzene, these were obtained perfectly pure and white. The results of an analysis were :

	Calculated for $C_{26}H_{20}$ .	Found.
C	93.97	93.82
H	6.03	6.3

The dihydride of di-phenyl-anthracene forms a white crystalline powder when crystallised from hot benzene, in which it is not very soluble. The crystals under the microscope are seen to be rhombic prisms. Its melting-point is 164.2°; its boiling-point 437°. It is insoluble in water, soluble in alcohol, ether, toluene and xylene.

Bromine in chloroformic solution does not act upon it in the cold. At the boiling-point of the chloroform, however, hydrobromic acid is given off, and by continuing the heating two hydrogen atoms may be replaced by bromine.



bromine were added to five grams dihydride of di-phenyl-anthracene dissolved in 200 cc. chloroform, and the chloroform kept vigorously boiling with reflux-condenser until hydrobromic acid ceased to pass off. The chloroform was now distilled off and the residue crystallised from alcohol. With one or two crystallisations it was possible to obtain a pure product.

An analysis gave:

	Calculated for $C_{26}H_{18}Br_2$ .	Found.
Br	32.65	32.47

Di-phenyl-anthracene bromide melts at  $127^{\circ}$  with slight decomposition. It crystallises from alcohol in small tablets. It is soluble in alcohol, benzene, chloroform and toluene.

The yield of dihydride of di-phenyl-anthracene is very small. From about 2000 grams of benzal chloride employed in the experiments only about 20 grams of dihydride of di-phenyl-anthracene were obtained.

CLARK UNIVERSITY, WORCESTER, MASS.

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## SOLID FORMULÆ; MODELS FOR USE IN TEACHING ORGANIC CHEMISTRY.

BY ARNOLD EILOART.

In lecturing on stereochemistry I have found models similar to those here described very helpful, and believe that they will prove useful also in general lectures on organic chemistry, elementary as well as advanced. These models do not pretend to represent any new conception as to the space-relations of atoms, but merely conveniently to represent established conceptions; further, they are not intended to supersede existing models, but to supplement them, for if only one sort of model be used there is danger that what is accessory may be considered essential; but when the same idea is represented by a variety of models it is seen that the essential is common to all, while variation of the accessories makes plain their non-essential nature.

That which is common to all models representing the space-relations of radicals attached to a carbon-atom is the prominence of four equidistant points; for although different radicals probably place themselves at different distances from the central carbon, they are for convenience represented as equidistant from it and from one another. Thus Van't Hoff used a regular tetrahedron, of which the centre and the four corners represented the relative positions of a carbon-atom and the radicals attached to it, a carbon-atom attached to unlike radicals being represented by a tetrahedron with the corners of different colors. The essence of the present device is the use of letters instead of colors at the corners

of the tetrahedra. As by means of caps fitting over the tetrahedron corners Van't Hoff could change their colors, so can the letter-symbols be changed by exchanging one cap for another. In addition, means are provided for supporting the tetrahedra so that the caps may be readily changed, for holding the cap on the corner it covers, for connecting the tetrahedra by one or by two corners, and for easy transition from the single to the double connection as well as *vice versa*.

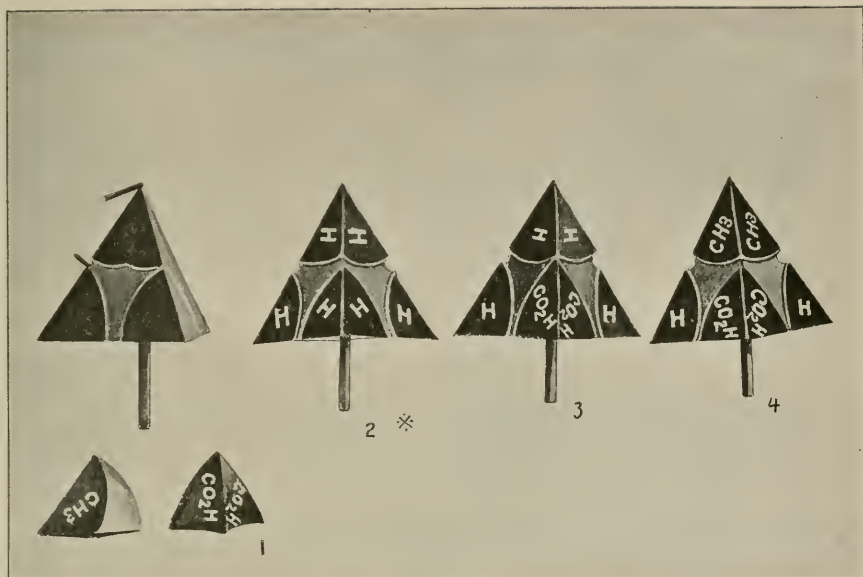
The figures (see Plates) show the arrangements.<sup>1</sup> It will be seen that when the tetrahedra are joined at one corner only the hinged connecting rod remains straight, because it sinks just so far into the lower tetrahedron that the hinge is covered. To convert the corner-connection (single-bond) into the edge-connection (double-bond), a pin is placed in the middle of that edge of the lower tetrahedron which is to be joined to the upper one, the latter is slightly raised, the little finger of the hand which raises it is used to lift the hinged rod till the hinge is free, and now any free corner of the upper may be made to touch the proper corner of the lower tetrahedron, and the pin will make the connection secure. This pin fits into the lower tetrahedron so tightly that it remains there when the edges are separated for restoration of the single-bond. These manipulations take a few seconds only. To test the durability of the arrangement by which the caps are held in place, some of them have been put on and off many times, one of them 300 times; all those tested work as well as when first used. To put a cap on and off takes less than a second.

### *The Use of the Models for illustrating General Organic Chemistry.*

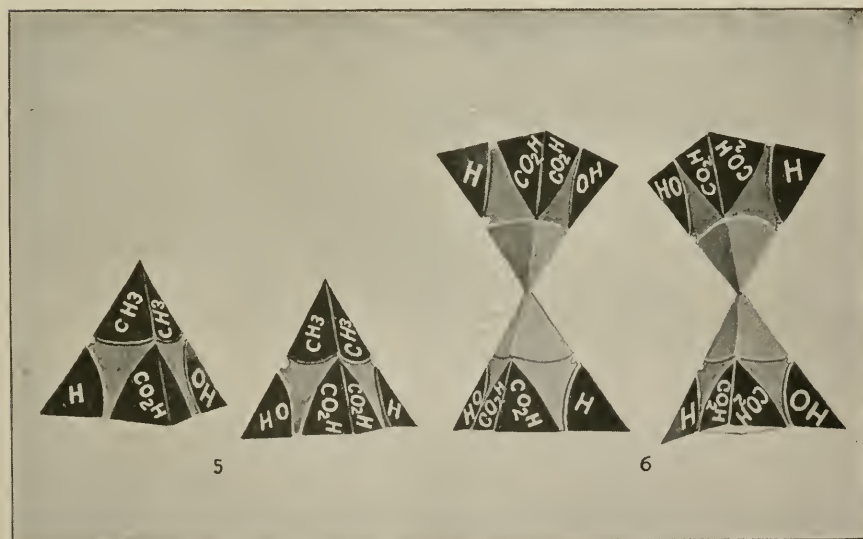
It is true that in using the models for this purpose our instructions are liable to become permeated with ideas as to the relative positions of atoms, ideas which we have not hitherto allowed to exert much influence on such teaching. But it is also doubtless true that an analogous statement could at one time have been made with regard to the introduction of structural formulæ. These, however, have long since emerged from the study of the investigator who, to make plain to himself his own conceptions, first used them, and now cover our blackboards. Similarly stereochemical models which already find a place on the study-

<sup>1</sup> The upright rods on which the models are supported have been omitted from the plates.

# PLATE I.



# PLATE II.



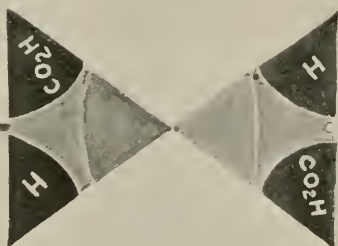






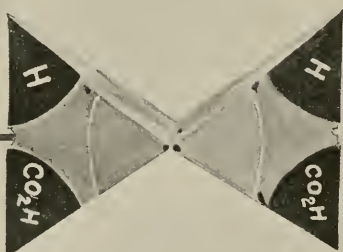
7X

7. Tartaric acid,  
inactive.



8X

8. Fumaric acid.



9X

9. Maleic acid.





tables of the few, must sooner or later cover our lecture-tables. Solid formulæ will partially supersede structural formulæ, as these have partially superseded empirical formulæ, and the gain in our power of concise and rapid thinking, similar in origin, will possibly be comparable in degree. As structural formulæ are more cumbersome to use than empirical, so are solid more cumbersome than structural formulæ; but in each case the more ample formula best stenographs our thought. And when a solid formula is once arranged it takes no more time to alter it, by exchanging one cap for another, than to turn to the blackboard and make the alteration in a written formula; in manipulating the models we have, too, the advantage of always facing the audience.

As to the dangers which are incident to the use of all formulæ, the history of stereochemistry shows that we must especially guard against proceeding faster than our knowledge warrants in the allotment of formulæ; on the other hand, the danger of cramping rather than stimulating thought is perhaps less formidable in the case of solid than of other formulæ.

It is well, however, in discussing the advantage of using solid formulæ, to consider particular cases. For instance, the fact that it is matter of indifference which hydrogen-atom in methane be exchanged for a given radical has been illustrated by means of the models of Kekulé;<sup>1</sup> the solid formulæ are equally effective, and with them we may illustrate the replacement of hydrogen by any given radical, and this without straining the memory to connect H, Br, CH<sub>3</sub>, etc., with the particular color assigned to it. Next, the cap marked CH<sub>3</sub>, which has represented methyl acting as an element, may be replaced by a block with three caps marked H; with the aid of this double means of representation the conception of a compound radical is readily imparted; similarly we may

develop  $\text{—C}_2\text{H}_5$  to  $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{—C—CH} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ , or to  $\begin{array}{c} \text{H} \\ | \\ \text{—C—CH}_3 \\ | \\ \text{H} \end{array}$ . The deriva-

tion of the series CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, etc., and of the general formula C<sub>n</sub>H<sub>2n+2</sub> is clearly seen; the tendency to ring-formation and the stability of rings of five or six carbon-atoms are explained at once.<sup>2</sup> Further, we may show the double- and the triple-linking of carbon-atoms; the diminution in the number of atoms bound by carbon-atoms so linked is represented by the impossi-

<sup>1</sup> See, however, Le Bel: *Bull. Soc. Chim.* [3] **3**, 788.

<sup>2</sup> See Plate in the report on Stereochemistry.

bility of covering by caps those of the tetrahedron corners which are in contact, and the formulæ  $C_nH_{2n}$  and  $C_nH_{2n-2}$  are deduced. Some of the facts mentioned might be represented by plane structural formulæ; but the representation of all the facts in the same way strengthens their connection in the mind.

*The Special Use of the Models in Stereochemistry.*

For a general explanation of the isomerism of compounds of the type  $CR^1R^2R^3R^4$ , the models of Kekulé or those of Van't Hoff may be used; it is when we have to deal with particular compounds (such, for instance, as the lactic acids) that we find the use of the models with letter-symbols desirable if not indispensable.

We may also not only show the general relations of radicals attached to two carbons singly-linked, the effect of the relative rotation of these carbons and of the inclination of the axes round which the two sets of radicals are ranged, but we may give solid formulæ to any compound of the type  $C_2R^1R^2R^3R^4R^5R^6$ ; we may show, side by side, the three solid formulæ for tartaric acid, how two of these together represent racemic acid, and how this acid is necessarily the product of the addition of four hydroxyl groups to two molecules of fumaric acid, while it is mesotartaric acid that must result from similar treatment of maleïc acid. The solid formulæ of fumaric and maleïc acid render Van't Hoff's theory as to their isomerism at once clear, and all the transformations attributable to their different configuration are traced with ease by means of the models. There are, in fact, but few configurations known to the stereochemistry of carbon which cannot be thus represented.

An objection to the particular form of model here described is yet to be noticed. The configurations of Wunderlich perhaps more nearly represent the truth than do those of Van't Hoff, and the former, it may be urged, should be taken into account in any attempt to extend the use of stereochemical models. Unfortunately, Wunderlich's configurations would require the use of transparent models in order that the formulæ of the radicals attached to the carbon-atoms might all be visible at once. Besides, the models described may be used to illustrate the general nature of the theories of Wunderlich, and they represent after all the four points equidistant in space about which Wun-



derlich's figures for the form of the carbon-atom are described. To illustrate further the theories of Wunderlich and Skraup<sup>1</sup> two large round-bottomed flasks may be used. The necks serve as handles, and four equidistant points on the outside of each flask are marked with colors or letters.

### *Details of Construction.*

The dimensions given need not be followed exactly ; but for every model the dimensions should be the same, so that the parts may be interchangeable.

The *tetrahedra*, 13 cm. (5 in.) in the edge, are cut from a long triangular prism of white wood 13 cm. in the side. At each corner is bored a hole of 0.5 cm. ( $\frac{3}{16}$  in.) in diameter and 4 cm. ( $1\frac{5}{8}$  in.) deep. Lining this and firmly fitted into it is a brass tube of 0.4 cm. ( $\frac{5}{32}$  in.) internal diameter, projecting only about 0.1 cm. Slight variation in the length projecting, in order to correct inequality in the length of the edges, is permissible. In the middle of each edge is bored a hole 0.5 cm. wide at the mouth and tapering to 0.3 cm. ( $\frac{1}{8}$  in.) at 0.3 cm. from the mouth ; the hole then continues 3 cm. ( $1\frac{1}{4}$  in.) deeper, the diameter of this part being adjusted to that of the rod which is to support the block. (A bill-file with loaded foot may be used.) In the middle of one face is bored a similar hole to fit the rod ; no enlargement at mouth. If many connected blocks are to be supported it is well to make in the middle of one face a hole large enough to receive the rod of a retort-stand having three feet.

The position of the grooves on the tetrahedron-faces is marked by drawing a line along the free edges of a cap pushed home on one of the tetrahedron-corners. The groove, which at its widest part is about 0.3 cm. across, slopes downwards towards the curve so described, where its depth is greatest—not more than 0.08 cm. ( $\frac{1}{32}$  in.) Six blocks suffice for most purposes, but for benzene-derivatives more will be necessary.

The *caps* are made of tin-plate about 0.5 mm. ( $\frac{1}{50}$  in.) thick, and measure about 6.3 cm. ( $2\frac{1}{2}$  in.) in the edge ; fitted on to a block, a cap then comes within about 0.5 cm. ( $\frac{1}{4}$  in.) of the centre of the block-edge. The cap is painted black, and on each of its three sides the symbol of the element or group for which it stands is

<sup>1</sup> Monatsh. Chem. 12, 146.

stencilled in white or gold.<sup>1</sup> It is well to have about forty caps, six marked H, four Cl, four Br, four I, four OH, two CH<sub>3</sub>, two C<sub>2</sub>H<sub>5</sub>, two C<sub>6</sub>H<sub>5</sub>, four COOH, and some caps unlettered for marking with chalk at will.

The *hinged rods* have each limb 3.5 cm. ( $1\frac{7}{16}$  in.) long, and are 0.3 cm. ( $\frac{1}{8}$  in.) thick, so that they slide freely in the brass tubes of the corner holes.

The *pins* are 2.5 cm. (1 in.) long, 0.5 cm. ( $\frac{3}{16}$  in.) thick in the middle, and taper down to 0.3 cm. at the ends. A pin pushed into one of the holes in the edge-centres must sink in a little more than half way; the part left outside the hole will then not fit a similar hole too tightly, so that another block may be put on and removed without disturbing the pin; that this may be done without allowing too much side-play to the blocks joined by the pin, care in adjusting the dimensions of the pins and holes is necessary.

The dimensions given are those of the models used by me; for a very large lecture-room larger blocks and caps would be necessary in order that the letters might be written larger; but blocks 15 cm. (6 in.) and caps 7.5 cm. in the edge would answer every purpose.

The work connected with this paper was done at Cornell University. I take this opportunity of expressing my thanks to Mr. Lester J. Young, instructor in Architecture, without whose valuable aid in word and deed it would have been hardly possible to bring the models to their present state.

NEW YORK, October, 1891.

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## THE EFFECT OF NASCENT HYDROGEN AND NASCENT OXYGEN ON NITRIC ACID.

BY WM. F. HALL.

In the periodic classification of the elements nitrogen is immediately connected with phosphorus, and rightly so, for there are many analogies between them. At the same time a most serious variance is found in their behavior toward oxygen. Phosphorus

<sup>1</sup> To protect the letters two small knobs of solder are placed on each face, one near each end of its free edge. The caps may then be packed one inside another without injury. This addition had not been made when the photographs were taken.

readily combines with this element to form oxides which, uniting directly with water, produce stable acids; whereas nitrogen combines with oxygen only when aided by a third substance or under extraordinary conditions, and the oxides form but one acid in any way stable. So great, indeed, is the difference in this respect that the question is legitimate whether nitrogen is in its proper place; and if it were shown that nitrogen could not form acids corresponding to those of phosphorus, it would not be unreasonable to refuse it its present position in the natural scheme.

The probability, however, is that nitrogen can form as many oxygen-acids as phosphorus, for every day, bringing announcements of new compounds, encourages the expectation that the nitrogen-acids in question will in due time be produced. Indeed, the most interesting bodies of recent discovery are two nitrogen hydrides, hydrazine and azoimid, or hydrazoic acid, having the formulæ  $N_2H_4$  and  $HN_3$  respectively.

The only stable acid of nitrogen at present known is nitric acid,  $HNO_3$ , which differs from the acid corresponding to the stable orthophosphoric acid,  $H_3PO_4$ , by a molecule of water. In solution then, so far as we know, a corresponding nitrogen-acid can exist, formed according to the reaction



Although all attempts at its isolation have failed, an examination by the freezing-method of Raoult would probably throw some light on the subject. This acid would be ortho-nitric acid, while the ordinary nitric acid would become the meta-acid. Similarly we should expect to have ortho-nitrous acid,  $H_3NO_2$ , which indeed we may expect to obtain by the addition of hydrogen to nitric acid, thus

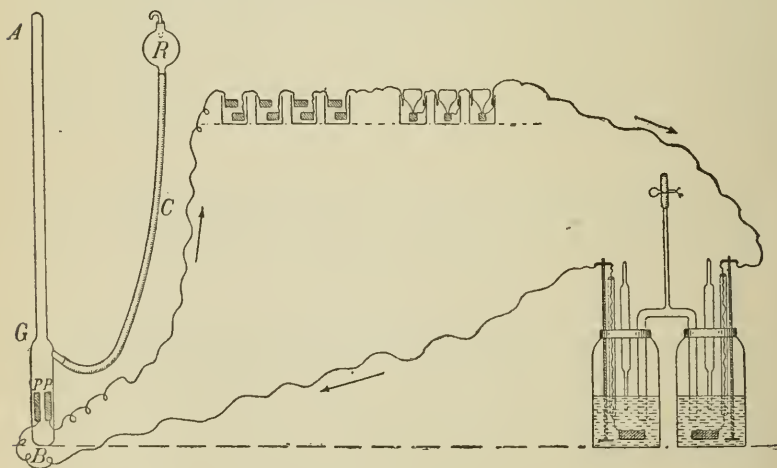


and doubtless, further, producing ammonia and the ammonium salt of hydrazoic acid. Wherefore a study of the action of nascent hydrogen upon nitric acid must throw light upon these compounds.

The following is an account of preliminary experiments to determine the conditions of action of nascent hydrogen on nitric acid. The results are principally negative, but nevertheless seem to be worth publishing, as at the end of the investigation, which had to be abruptly terminated at the close of the session, some interesting results were indicated. At the same time the action of nascent oxygen on nitric acid was observed.

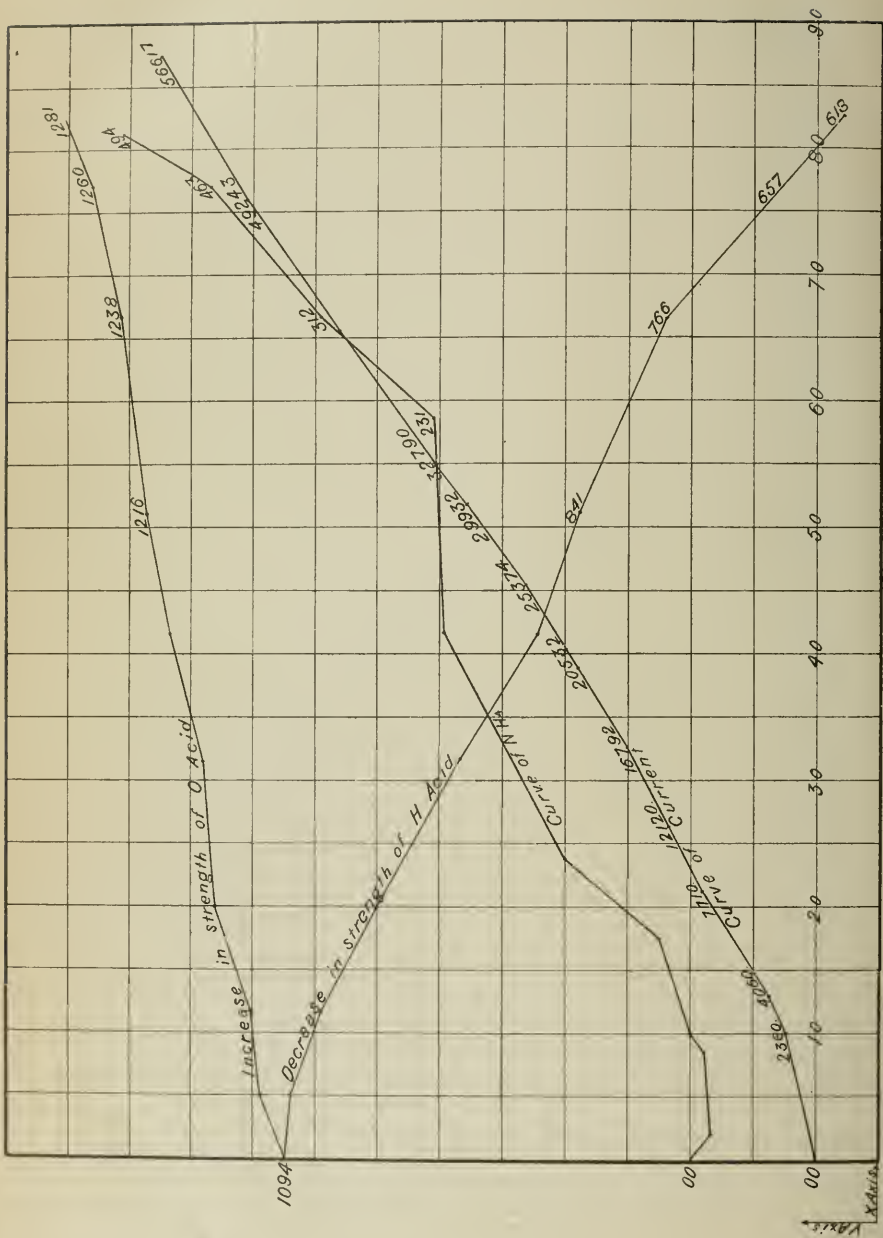
Decomposition by means of electricity presented the most favorable way of simultaneously obtaining the nascent gases. The apparatus and arrangement was as follows: The two glass jars containing the electrolyte were each about 7 in. high by 4 in. in diameter, connection between them being made by a tube,  $\frac{1}{2}$  in. in diameter, bent thus  $\cap$ , the upright arm being a tube of much smaller bore, closed by rubber tubing and a pinch-cock, so that by releasing the pinch-cock the liquid in the connecting-tube would fall, thus breaking connection. Through the cork closing each jar extended the conducting-wire, protected from the acid by glass tubing; a 5-cc. pipette and a glass stirrer, the lower end of which was curved into a spiral so that the liquid might be thoroughly agitated. The platinum electrodes, not covered with platinum black, were  $1\frac{5}{16} \times \frac{1}{16}$  in. After carefully cleaning and somewhat roughening the surfaces in order that the gas might freely escape, they were placed with the flat sides vertical.

The decomposing current was 303 milli-amperes per square centimeter of surface of the electrode, with an electromotive force of about 7.5 volts. Three Meidinger flask-cells were at first tried in series, the connecting-tube being then only  $\frac{3}{16}$  in. in diameter; the current was not sufficiently strong until the number of the cells had been increased to seven and the connecting-tube exchanged for one of  $\frac{8}{16}$ -in. diameter. The accompanying sketch will show the arrangement of the apparatus.









To measure the current a gas-voltameter was chosen because of its convenience. The tube was carefully calibrated with mercury, and a table of the graduations so arranged that a reading of the level of the liquid gave directly the current that had flowed since filling the tube.

In the sketch, *AB* is the tube, graduated from *A* to *G*. The gas-exit was placed some distance above the electrodes and, the bore of the lower portion of the tube being quite large, the electrodes were never exposed. These electrodes were  $2 \times \frac{5}{16}$  in. The voltameter was so clamped in an upright position that it might be partially inverted, thus allowing the gas to escape and the tube to be refilled from the reservoir *R*, through the rubber tube *C*.

According to Mascart (see Stewart and Gee), the use of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in a voltameter will prevent the formation of ozone; for that reason phosphoric acid, diluted with water, 3 to 10, was used. Before using the voltameter, gas was passed through the liquid for several days, to saturate it. The tube allowing the gas to escape from the reservoir *R* was very small and bent downward to retain some of the electrolytic gas and keep the liquid covered with it.

Into each electrolytic cell were put 100 pipettefuls, 491.14 cc. or 527.51 grams nitric acid, containing 0.0124128 gram  $\text{NO}_3$  per cc. The current passing through the cells released oxygen in the one and hydrogen in the other. The electrolyte was tested from day to day as follows:

- (1). Measure the current.
- (2). Stir the liquids thoroughly.
- (3). Withdraw one pipetteful and titrate with barium hydroxide.
- (4). Test for nitrous acid with iodised starch solution.
- (5). Test for ammonia with known excess of barium hydroxide.

From the results of these measurements the accompanying curves were platted.

### *Curve of Current.*

The *y*-axis indicates the quantity of current that has acted on 100 cc. of the electrolyte since the connection was first made, March 9, 1891; this quantity being easily determined by dividing the quantity of current that flowed through the liquid in either jar by a number that would reduce the liquid in that jar to 100 cc., the amount of liquid in either jar being always known.

The  $x$ -axis is on the scale of one day per two divisions; the  $y$ -axis is on the scale of 500 coulombs per division.

The curve approximates a straight line, showing that the flow of current was quite steady and that the conductivity has changed but slightly, if at all, except on the tenth day, when the curve bends abruptly upward, owing to a removal of 100 ohms resistance, which confirms the opinion that the conductivity did not change very much, as such a change in resistance produces a large change in the current. Although the current was steady and constant, the decomposition was accompanied by curious phenomena.

Had no action taken place within the liquid, two volumes of hydrogen should have escaped for one volume of oxygen, but for several days after the apparatus was put in order it was easily seen that the flow of oxygen was largely in excess. Within a few days, however, the flow of hydrogen had apparently increased to the proper proportions. These rates of flow continued with little or no change until the fifty-ninth day, when it was noticed that the flow of hydrogen had almost ceased, while the flow of oxygen seemed unchanged. From the fifty-ninth day to the eighty-fourth day—that of last observation—the flow of hydrogen was very small, at times only a very few pin-point bubbles arising. The oxygen flow decreased gradually, but at no time became as small as the hydrogen flow.

Particular attention is called to the fact that after the fifty-ninth day the flow of gases was largely increased when the liquids were agitated; especially is this true of the hydrogen. Within a few hours the flow decreased to the amount that was given off before the agitation.

The titration indicated that the oxygen-liquid increased in acidity and the hydrogen-liquid decreased.

#### *Curve of Increase in Strength of Oxygen-Acid.*

With the same time-ordinate as before, but with the  $y$ -axis representing the increase in the amounts of barium hydroxide required to neutralise the oxygen acid, the curve of increase in strength of 100 cc. of the oxygen-liquid was platted. The increase in strength is due to the concentration of the electrolyte, with the transference of the ions, thus continually forming more nitric acid; and possibly to the formation of orthonitric acid,  $\text{H}_2\text{NO}_4$ .

Ammonium salt in minute quantity was detected by test-paper;

the quantity seemed slowly to increase, but at no time exceeded a trace. The presence of ammonium salt in this cell is probably due to the mixing of the liquids through the connecting-tube, thus introducing the salt from the hydrogen cell. The presence of nitrous acid ( $\text{HNO}_2$ ) was not detected. The curve shows that the increase in strength has been slow but constant; the removal of the 100 ohms resistance the tenth day may be the cause of the more rapid increase in strength of the acid.

*Curve of Decrease in Strength of the Hydrogen-Acid.*

With the same ordinate as before, the curve showing the decrease in strength of the hydrogen-acid was platted, with the  $y$ -axis representing the amount of barium hydroxide required to neutralise 100 cc. of the liquid. The decrease in strength is due to decomposition of the electrolyte with transference of the ions and to the formation of ammonium salt. The ammonia steadily increased, but at no time was present in such quantity that it could be determined quantitatively. Owing to the formation of the ammonium salt and the transference of the ions, the hydrogen-liquid decreased in acidity more rapidly than the oxygen-liquid increased. The rapid descent of the curve after the tenth day is probably due to the removal of the 100 ohms resistance.

The curve of increase and the curve of decrease begin at the same point—the amount of barium hydroxide required to neutralise 100 cc. of the electrolyte before the current was started. The  $y$ -axis is platted on a scale of 5.5 cc. of barium hydroxide per division. The  $x$ -axis of each curve is platted on the scale of one day per two divisions.

The barium hydroxide used throughout this experiment was of such strength that 1 cc. equaled 0.9616 gram  $\text{NO}_2$ .

*Curve of Ammonium Salt.*

This curve, too, is platted for 100 cc. of the electrolyte with the same time-ordinate as before and the  $y$ -axis for milligrams  $\text{NH}_4$ , 5.5 milligrams per division. Assuming that the increase in strength would have equaled the decrease, but did not because of the formation of ammonium salt, the barium hydroxide required to neutralise 100 cc. of the oxygen-liquid is added to that required to neutralise 100 cc. of the hydrogen-liquid; the result is divided by 2 and the quotient subtracted from 1094, the number of cc. of

barium hydroxide required to neutralise 100 cc. of either acid at the beginning of the experiment. This difference is the amount of barium hydroxide that would have been required to neutralise the amount of nitric acid that had been neutralised by the formation of ammonium salt and also that consumed in the production of ammonia.

At the first the curve dips down, but soon turning upward proceeds in an irregular manner.

The peculiar action at the hydrogen-electrode since the fifty-ninth day indicates that important results would be reached by continuing the experiments, but the close of the session stopped further work.

The liquids then stood as follows: the oxygen-liquid had a specific gravity of 1.079 at 27° C., the hydrogen-liquid a specific gravity of 1.034 at 27° C.: at the beginning the specific gravity of the nitric acid was 1.069 at 20° C. The hydrogen-liquid decreased rapidly but regularly in strength; ammonium salt was formed slowly but with increasing rapidity in the hydrogen-liquid. Hydrazoic acid was not found.

The oxygen-liquid increased in strength very slowly, but no other change was observed. The quantity of ammonium salt was so small that all of it was probably brought from the hydrogen cell by the currents of liquid.

STATE UNIVERSITY OF MISSOURI, *June, 1891.*

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## NOTE ON THE ELECTROLYTIC DETERMINATION OF METALS AS AMALGAMS.

BY WOLCOTT GIBBS.

In a paper read before the National Academy of Sciences, in October, 1883, I gave an account of a method of electrolysis for the separation of metals from their solutions by the employment of metallic mercury as negative electrode, the positive electrode being a plate of platinum. Under these circumstances and with a current of moderate force I found it possible to separate iron, cobalt, nickel, zinc, cadmium and copper so completely from solutions of the respective sulphates that no trace of metal could be



detected in the liquid. In addition I found that phosphates of these metals dissolved in dilute sulphuric acid were easily resolved into amalgams and free acid, and I pointed out the advantage of the method in at least a certain number of cases. The process attracted the attention of chemists who were present at the meeting and was noticed in several of the daily papers. It was also noticed in the *Zeitschrift für Analytische Chemie* 22, 558, and in the *Chemical News* 42, 291. I had in view both the determination of the metal by the increase in weight of the mercury, and in particular cases of the molecule combined with the metal, either by direct titration, or by known gravimetric methods. It is but just to those chemists who have since studied the method to state that my experiments were purely qualitative, such being in my opinion sufficient to establish the correctness of the principle involved.

The method is described in Prof. Edgar F. Smith's work<sup>1</sup> on electro-chemical analysis, but it is incorrectly stated that it was applied to tin and mercury. I made no experiments with either tin or mercury. In 1886, two years after the presentation of my paper to the National Academy, Luckow<sup>2</sup> applied the same process to the estimation of zinc. Very recently Prof. T. M. Drown<sup>3</sup> has shown that the quantitative separation of iron from even very small quantities of alumina may be effected by electrolysis with mercury, the results being very satisfactory. It is to be expected that the process will give equally good results in the separation of iron and some other metals from titanium, zirconium, niobium and tantalum.

Very recently the subject has been taken up by Vortmann,<sup>4</sup> who has made numerous quantitative experiments with mercury, zinc, cadmium, lead, bismuth and antimony. The numerical results obtained, if not extremely accurate, are at least fairly good. It is to be hoped that the determination quantitatively of the electro-negative atoms or molecules united with the metal will also attract attention, the method having been originally intended to serve the double purpose. The inaccurate statements which have been made as to my own share in the invention of the process have led to the publication of this note.

NEWPORT, R. I., Nov. 1, 1891.

<sup>1</sup> *Electro-chemical Analysis*, by Edgar F. Smith. Philadelphia, 1890.

<sup>2</sup> *Ztschr. anal. Chem.* 25, 113, 1886.

<sup>3</sup> *Transactions of the Institute of Mining Engineers* 20 (not yet published), 1891.

<sup>4</sup> *Ber. d. chem. Ges.* 24, 2749.

## SAPOTIN: A NEW GLUCOSIDE.

BY GUSTAVE MICHAUD.

*Achras Sapota*, L., is a large tree scattered through the forests of Central America and the West Indies; its fruit is often seen upon the Creole dinner-table. This fruit is a berry, the size of an orange, the taste of which suggests the flavor of melon, as well as that of hydrocyanic acid. The fruit contains one or two seeds like large chestnuts, which if broken let fall a white almond. This last contains the glucoside which I call *sapotin*.

I obtained sapotin for the first time by heating dry raspings of the almond with 90-per cent. alcohol. While cooling, the filtered liquid deposited a good deal of the compound. Since that time I have advantageously modified the process and increased the amount of product. I prepare sapotin in the following way: The almonds are rasped, dried at 100° C. and washed with benzene, which takes away an enormous quantity of fatty matter. The benzene which remains in the almond is driven out first by compression, afterwards by heating. Then the raspings are exhausted with boiling 90-per cent. alcohol. The solution is filtered as rapidly as possible, in order to avoid its cooling and depositing the sapotin in the filter. As soon as the temperature of the filtered liquid begins to fall, a voluminous precipitate is seen to form, which is the sapotin.

In order to purify it, the precipitate is collected in a filter and expressed between sheets of filter-paper. When dry it is washed with ether, which takes away the last particles of fatty and resinous matter. The purification is completed by two crystallisations from 90-per cent. alcohol. At last the substance is dried at 100°.

The sapotin separates from its alcohol solution in the form of microscopic crystals. When dry, it is a white, inodorous powder. Its taste is extremely acrid and burning. If the powder penetrate into the nostrils or the eyes it produces a persistent burning sensation which brings about sneezing and flow of tears. It melts at 240° C., growing brown at the same time.

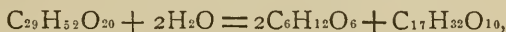
It has a laevo-rotatory power of  $[\alpha]_D = -32.11$ , which was determined with an alcoholic solution, the aqueous solution not being sufficiently transparent.

It is very soluble in water, easily soluble in boiling alcohol, much less in cold alcohol, and insoluble in ether, chloroform and benzene. Its alcoholic solution is precipitated by ether.

Tannin has no action on it, but basic acetate of lead produces a gelatinous precipitate in its aqueous solution. Strange enough, this precipitate is entirely soluble in a small excess of basic acetate of lead. If thrown into concentrated sulphuric acid, sapotin colors it with a garnet-red tint. It does not reduce Fehling's solution. Its analysis gave the following results:

	Calculated for $C_{29}H_{52}O_{20}$ .	I.	Found.	II.
C	48.33	48.69		48.31
H	7.23	7.33		7.45

When heated with water and a little sulphuric acid, sapotin is decomposed and yields glucose and an insoluble matter which I call *sapotiretin*. 100 parts of sapotin produce 51.58 parts of glucose and 49.67 of sapotiretin. The equation which represents this reaction is—



and requires 50 per cent. of glucose and 55 per cent. of sapotiretin.

Sapotiretin is an amorphous compound, insoluble in water, very soluble in alcohol, less soluble in chloroform, insoluble in ether. Below is the result of its analysis:

	Calculated for $C_{17}H_{32}O_{10}$ .	I.	Found.	II.
C	51.52	51.21		51.20
H	8.08	8.19		8.34

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## REVIEWS AND REPORTS.

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### STEREOCHEMISTRY.

(Continued from p. 504.)

#### *The "Strain" Theory of Von Baeyer.*

A striking characteristic of Van't Hoff's explanation of the isomerism described at the close of the first part of this paper<sup>1</sup>

<sup>1</sup> This Journal 13, 503.

is the spontaneity with which that explanation flows from the original Tetrahedron Hypothesis. With equal readiness does this hypothesis lend itself—as was first shown by Van't Hoff—to the explanation of ring-formation and the superior stability of rings of five or six carbon-atoms. Later Von Baeyer<sup>1</sup> attempted a similar explanation, adding this hypothesis: "The four valences of a carbon-atom act in the direction of the lines connecting the center of a regular tetrahedron with the apices, lines which are at an angle of  $109^{\circ} 28'$  with one another. The direction of the attraction can undergo a divergence, which, however, is attended by a proportional strain." In acetylene, *e. g.*, the three valences connecting the carbons are all diverted from *Ca* to *CC* (Fig. 9); hence

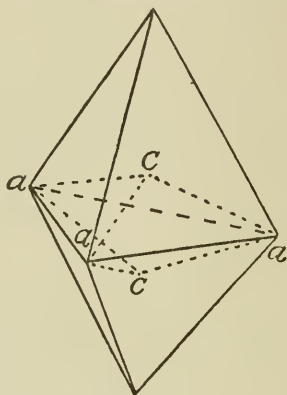
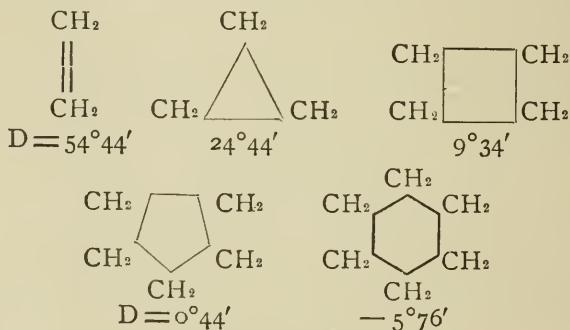


FIG. 9.

the negative heat of formation of acetylene, and the explosive nature of its compounds, and especially of polyacetylene compounds. The greater the divergence, the greater the strain; the greater the strain, the less the stability. Of the different methylene-rings the five and six carbon-rings show the least divergence (*D*) of their valences from the angle  $109^{\circ} 28'$ .



<sup>1</sup> Ber. d. chem. Ges. 18, 2277.

In these, then, the strain is least, and therefore it is that they are the most stable. Moreover, König<sup>1</sup> maintains that the pentamethylene is more stable than the hexamethylene ring.

Naumann<sup>2</sup> has given an explanation of the weakness of the triple- and double-bonds which differs from that of Von Baeyer. He supposes that of the affinity-force directed towards the corners of two carbon-atoms, only the component which acts in the line joining the tetrahedron-centers is effective in holding the two

atoms together. Calling this for  $\begin{array}{c} \text{C} \\ | \\ \text{C} \end{array} = 1.0000$ , it will be for  $\begin{array}{c} \text{C} \\ || \\ \text{C} \end{array} = .5774 \times 2$  and for  $\begin{array}{c} \text{C} \\ ||| \\ \text{C} \end{array} = .3333 \times 3$ . The force required to break

one bond will be, then, for  $\begin{array}{c} \text{C} \\ ||| \\ \text{C} \end{array} > .3333$ , for  $\begin{array}{c} \text{C} \\ || \\ \text{C} \end{array} > .5774$ , and for  $\begin{array}{c} \text{C} \\ | \\ \text{C} \end{array} > 1$ .

Von Baeyer<sup>3</sup> rejects this explanation, saying that the affinities may be represented by elastic wires, the bending of which causes a strain not taken into account by resolving the attractive force according to the parallelogram of forces. The "strain" theory also has been criticised.<sup>4</sup> In fact, according to the valence hypothesis of V. Meyer and Riecke,<sup>5</sup> it is unnecessary to assume a divergence of valences in acetylene. Besides, we can form in connection with the mutual attraction of atoms no conception of that which corresponds to Von Baeyer's elastic wires.<sup>6</sup>

### *The Theories of Wunderlich and of Skraup.*

A mode of representing the linkage of carbon-atoms which is free from the objections just mentioned is given by Wunderlich.<sup>7</sup> It is based on an hypothesis as to the form of the carbon-atom. Van't Hoff had offered no suggestion as to this; with him, the tetrahedron is merely the form enclosed by lines joining the points which radicles attached to a carbon-atom occupy relatively to one another. Wislicenus<sup>8</sup> thinks it possible that this tetrahedron represents the form of the carbon-atom, the attractive force of the atom being concentrated at the apices; so that where there is least matter there is most force. Wunderlich, however, conceives the atom as having at least some matter round its binding-points, probably as much as anywhere else; so that the atom may be spherical, *e. g.*; or the atom-substance may be concentrated

<sup>1</sup> Chem. Centrbl. 1890, 1, 788.

<sup>2</sup> Ber. d. chem. Ges. 23, 477.

<sup>3</sup> Ber. d. chem. Ges. 23, 1272.

<sup>4</sup> Ibid. 23, 581.

<sup>5</sup> Ibid. 21, 949.

<sup>6</sup> Comp. Auwers, "Entwicklung der Stereochemie" (Heidelberg, 1890), pp. 18 and 25. See also p. 152, where V. Meyer gives reasons for doubting whether the double and triple bonds are really weaker than the single bond.

<sup>7</sup> "Configuration organischer Moleküle" (Würzburg, 1886); or see Auwers, "Entwicklung," pp. 18 *et seq.*

<sup>8</sup> Ber. d. chem. Ges. 21, 584.



behind the binding-points so that the form of the atom may be a regular tetrahedron, but with the binding-points in the centers of the faces. The atom-form would be represented in the former case by the sphere, in the latter by the tetrahedron circumscribed about the tetrahedron of Van't Hoff or Wislicenus. In any case—and this is the essential hypothesis—the atom-substance is conceived as so disposed between the binding-points that the single-link between two carbon-atoms is the only connection permitting of actual contact of binding-points. Let us consider, for example, the tetrahedra of Wunderlich. Singly-linked, these would be face to face, two binding-points would touch; doubly-linked, they would have two pairs of faces opposed or would be edge to edge; trebly-linked, three faces of one would be opposed to three of the other, or the tetrahedra would be point to point. Assuming these positions, and that the attraction varies inversely as the square of the distance between the binding-points concerned, Auwers<sup>1</sup> calculates the ratio of the strength of the double-link to that of the triple-link to be 3.56:1. If the atoms are not tetrahedra, but spheres, the ratio is 1.65:1.

When the tetrahedra of Wunderlich form saturated rings, the singly-linked faces can no longer touch; their angle of inclination is least for five-carbon rings, and increases as the number of carbon-atoms differs from five; so that here too we have a very simple representation of the facts.

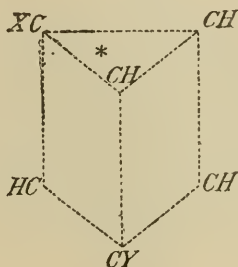
Again, since in the doubly-linked tetrahedra the binding-points do not touch, oscillations causing them to approach and recede are possible. Suppose such oscillations to take place in the plane of the four binding-points concerned. Then atoms capable of forming an addition-product will attach themselves to the binding-points which have receded, and are therefore now less nearly saturated; the approaching points continuing to approach till they touch; *i. e.*, addition of elements to doubly-linked carbons will usually break one bond, not both, as would be the case if the two were permanently equal. But owing to the oscillations, addition is as likely to take place on one side of a molecule as on the other; *i. e.*, from fumaric acid we get as many molecules of right- as of left-handed tartaric acid, not all right- or all left-handed acid, as would be the case if the two bonds were permanently unequal. This ingenious modification of Wunderlich's conception is due to Skraup.<sup>2</sup> One comment may be permitted: the oscillations assumed involve recession of the two binding-points which have approached (whose attraction should therefore be increased), and approach of the two binding-points on the other side which have receded (whose attraction should therefore be diminished). Thus the oscillation-hypothesis is in conflict with the hypothesis that the attraction between two binding-points increases as the distance between them diminishes.

<sup>1</sup> "Entwicklung," p. 33.

<sup>2</sup> Monatsh. Chem. 12, 146.

*The Configuration of the Benzene Molecule.*

The discussion of this problem has involved the application of most of the theories which have been sketched. The later theory of Van't Hoff, that every C group is optically active, has been used to determine the choice between conflicting benzene formulæ. If two ortho-hydrogens in benzene are replaced by different radicles, we have, according to the prism-formula, an asymmetric carbon-atom (marked \*).



But no substitution-product of benzene is active, nor has any been rendered active even by the action of ferments. The preference must therefore be given to a formula like that of Kekulé, showing the carbons with double-bonds or with central valences. Such a formula is in accordance with the fact that only addition-products of benzene are active.

An attempt has been made to apply also the theory peculiar to Le Bel. Since, according to this, *any* asymmetric molecule is active, every benzene derivative in which three hydrogens are substituted should, it is said, be active unless these hydrogens occupy a plane of symmetry of the molecule.<sup>1</sup> The absence of active substituted benzenes proves, therefore, that all the hydrogens are in a plane of symmetry of the molecule. According to Van't Hoff,<sup>2</sup> it proves also that all the carbon-atoms are in the same plane. Herrmann,<sup>3</sup> however, does not regard this as a necessary consequence. He gives a formula for benzene, in which the six carbons are divided into two groups, occupying two planes parallel with the plane of the hydrogen-atoms and equidistant from it.

No carbon-atom of one group is opposite a carbon-atom of the other; but the centers of gravity of the two groups are opposite and balance one another about the central plane containing the

<sup>1</sup> This reasoning, however, like that by which the formula for methane was deduced, is based on the unproved assumption that the radicle substituted for a hydrogen-atom takes the place previously occupied by that atom.

<sup>2</sup> Loc. cit. p. 81.

<sup>3</sup> Ber. d. chem. Ges. 21, 1958.

hydrogen-atoms. Thus any optical activity due to one of the groups will be counterbalanced by the opposite activity of the

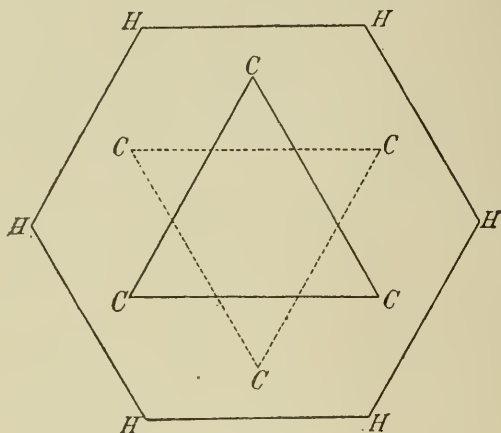

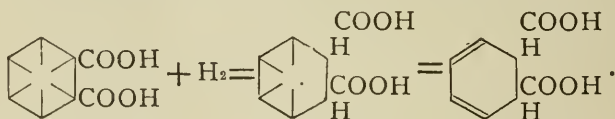


FIG. 10.

opposite group. Von Baeyer's investigation of the constitution of benzene—a result of his strain-theory—led him to the space-

formula shown in the figure<sup>1</sup> (Plate I). The formula  had

already been proposed by Armstrong.<sup>2</sup> It is the ground-plan of the other with the middle left out, and both are intended to show that no one of the central valences monopolises any other, but all "mutually paralyse one another" (Von Baeyer). The valences are potential, not active. The linking of the carbon-atoms is stronger than any that exists in rings without central valences, and as Bamberger<sup>3</sup> shows for aromatic rings in general, the difference ceases directly the equilibrium of the central valences is disturbed by formation of addition-products. The potential valences become active. For instance, in the reduction of phthalic acid,



See Plate I.<sup>4</sup>

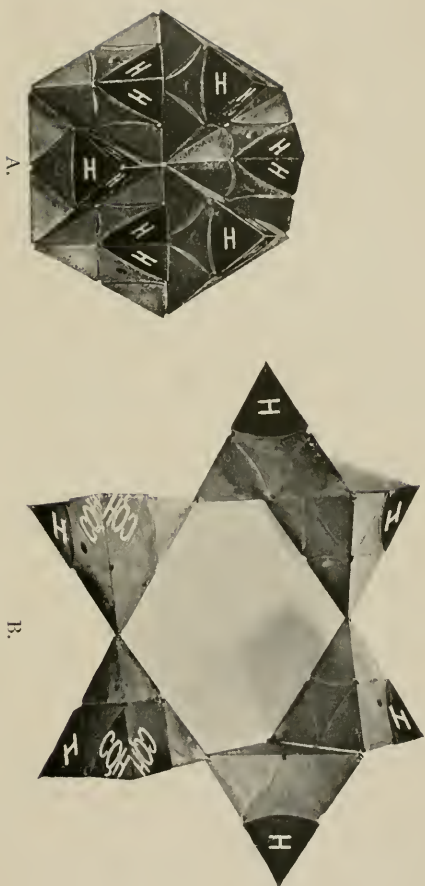
<sup>1</sup> Loschmidt (*Monatsh. Chem.* **11**, 28) reproduced this formula two years later to account for the formation of benzene from acetylene.

<sup>2</sup> *J. Chem. Soc.* **51**, 264.

<sup>3</sup> *Ann. Chem.* (Liebig) **257**, 1 (1890). The theoretical conclusions of the paper had been to large extent anticipated by Marsh (*Phil. Mag.* 1888, **2**, 426).

<sup>4</sup> The formula given probably represents not the existing dihydro-phthalic acid, but an isomer. (Von Baeyer, *Ann. Chem.* **258**, 160.)

PLATE I.



- A. Benzene (Baeyer's formula; the models are seen from above).  
 B. Dihydrophthalic acid.

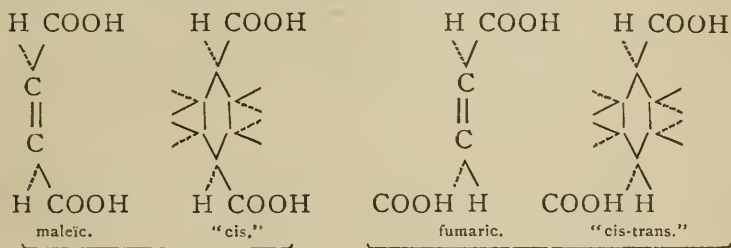
For a description of the models, see the article on "Solid Formulas" in this number of the Journal.





In opposition to the central formula, Ladenburg<sup>1</sup> maintains that it lacks a mechanical basis; that the valences of two diagonally opposed carbons being equal and opposite, must mutually saturate each other, so that no part of their attractive force can be engaged with any other central valence; but this is saying that each pair of diagonally opposed carbons is linked in the ordinary way, *i. e.*, that the central formula is equivalent to Claus's diagonal formula.

A remarkable link between the stereochemistry of rings and that of the double-bond was found by Von Baeyer in the two hexahydro-terephthalic acids, called by him "cis" and "cis-trans." In appearance and in solubility these acids mimic maleic acid and fumaric acid respectively; moreover, the less stable maleoid acid readily passes into the more stable fumaroid acid. The analogy is completely represented by the formulæ<sup>2</sup>



and was foreseen by Van't Hoff in 1875.

Sachse<sup>3</sup> objects to these formulæ that they do not account for the conversion of "cis" to "cis-trans" acid *in the cold*, and he suggests another space-formula for hexamethylene, which is easily derived from his formula for benzene;<sup>4</sup> and Herrmann<sup>5</sup> protests against all attempts to arrive at the formula of hexamethylene or of benzene by the placing together of tetrahedra, and points to the impossibility of representing the formation of benzene from acetylene by a multiplication of the space-formula of the latter.

<sup>1</sup>Ann. Chem. (Liebig) **246**, 382; Ber. d. chem. Ges. **23**, 2688. Compare also Claus: J. prakt. Chem. [2] **40**, 69, and **42**, 24; and Von Baeyer's answer to him: Ann. Chem. (Liebig) **258**, 145; also Bamberger's: J. prakt. Chem. [2] **42**, 118.

Wachter (Chem. Centrbl. 1890, **1**, 457) has given a compact review of the evidence for the various benzene-formulæ, including the space-formulæ.

<sup>2</sup>The dotted lines are supposed to be on one side, the corresponding solid lines on the other side of the plane of the ring. Other cases of this isomerism are the benzene hexachlorides (Friedel: Bull. Soc. Chim. [3] **5**, 130; abstract: This Journal **13**, 356), the thioaldehydes (Baumann: Ber. d. chem. Ges. **24**, 1419, compare Figs. 45 and 46 in Van't Hoff's "La Chimie dans l'espace," 1875); and the menthols (Beckmann: Ann. Chem. (Liebig) **250**, 322). See also p. 87 of "Chemistry in Space," a translation by Marsh of the "Dix Années," with additions by Van't Hoff (Oxford, 1891, Clarendon Press).

<sup>3</sup>Ibid. **23**, 1363.

<sup>4</sup>Ibid. **21**, 2530; abstract: This Journal **11**, 132. Compare, however, Herrmann: Ber. d. chem. Ges. **23**, 2060, and Auwers, "Entwicklung," p. 51.

<sup>5</sup>Ber. d. chem. Ges. **23**, 2060.

*Development of the Theory concerning Unsaturated Isomers by Wislicenus.*

The explanation of isomerism of the fumaric-maleïc type, resulting from the space-formula for ethylene, though published by Van't Hoff in 1874, began to hold and dominate chemical thought on these subjects only when, in 1887, the work of Wislicenus<sup>1</sup> rendered the theory amenable to the test of experiment. Hence much of Van't Hoff's theory is sometimes<sup>2</sup> ascribed to Wislicenus. And this is not remarkable, since the ideas of Wislicenus grafted themselves so naturally on the theory of Van't Hoff, and the offshoots of both are so intricately interlaced, that it is difficult to distinguish at all points between the earlier and the later growth. For Wislicenus introduced but one additional hypothesis, and with the further aid of one simple and well-recognised principle he then followed out logically and applied systematically the hypotheses of Van't Hoff. Van't Hoff had said that two trebly-linked carbons are represented by two tetrahedra face to face. Wislicenus said: It follows that any two monad radicles added to these will be on the same side of the molecule.

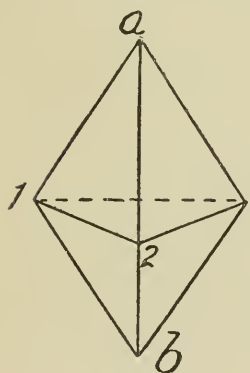


FIG. 11.

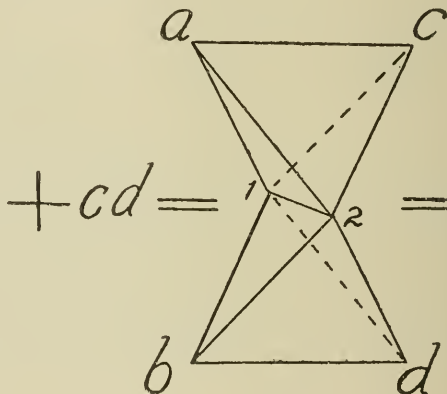


FIG. 12.

The principle here is that of least disturbance: no more bonds are to be broken than is necessary to effect the transformation. The same principle was applied to the change from the double to the single bond. Again, Van't Hoff had said that two carbon-atoms singly-linked might rotate in opposite directions round the axis joining their centers, but for the fact that they are held in one position by the affinity of the groups attached to the one

<sup>1</sup> "Ueber die räumliche Anordnung der Atome in organischen Molekülen und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindungen." Leipzig, 1887; 2d ed. 1889.

<sup>2</sup> Compare, *e. g.*, Pattison Muir, *loc. cit.* pp. 182 and 183.

for the groups attached to the other; the position of equilibrium depending for each compound on the nature of the groups, and being left undetermined. Wislicenus said that with the aid of

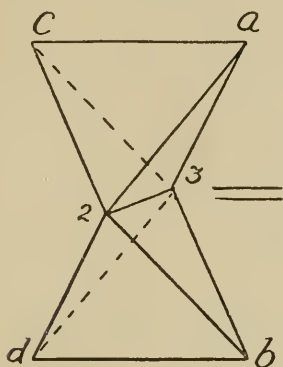


FIG. 13.

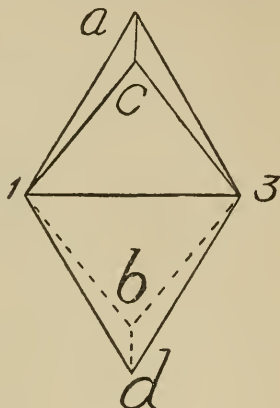


FIG. 14.

the hypothesis that the greater the difference in "positivity" or "negativity" the greater the affinity between two radicles, we could for many compounds determine the position of equilibrium. Thus of the three configurations for malic acid the third is the

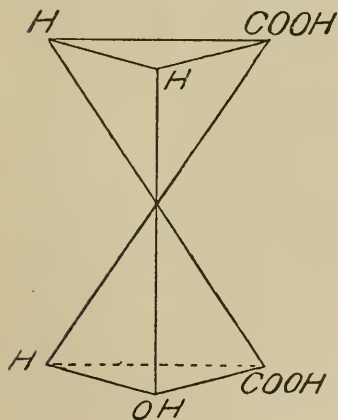


FIG. 15.

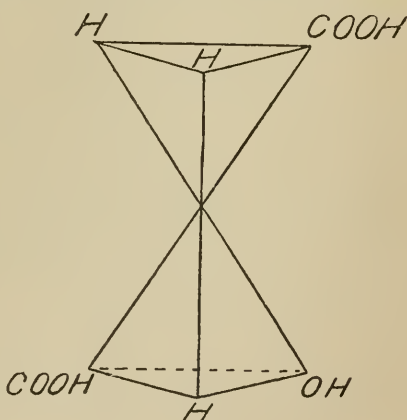


FIG. 16.

stable configuration, and the other two, if formed, would immediately by rotation be converted into it. But this state of affairs may be modified by the atomic motion due to heat, until at a

sufficiently high temperature all the relative positions possible for the radicles H, H, COOH with regard to H, OH, COOH, may be realised successively at equal intervals of time. As Van't Hoff

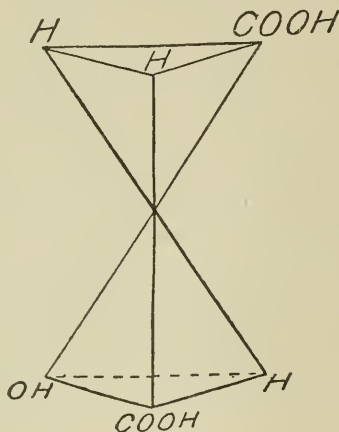


FIG. 17.

observes with regard to the way in which the validity of inferences from the theory may be affected by the action of heat: "Throughout, our theory can represent the reality only as this would be at absolute zero" (p. 88).

In the case of the formation of a non-saturated from a saturated compound, we are aided in fixing the position of our six radicles by the fact that the two radicles leaving the molecule—the two whose simultaneous action causes the change—must be opposite to each other—in "corresponding positions"—at the moment of the change. This necessity and the affinities of the radicles of the saturated compound often indicate the position of the radicles in the unsaturated compound formed. It was the positions of the radicles in unsaturated isomers which Wislicenus wished to determine, and we can best illustrate his theories and those of Van't Hoff by applying them to two ethylene derivatives—

fumaric and maleic acids,  $\begin{array}{c} \text{CH COOH} \\ || \\ \text{CH COOH} \end{array}$ . From what has been

said it follows—(1), that the acid formed by the addition of  $\text{Br}_2$  to  $\begin{array}{c} \text{C COOH} \\ ||| \\ \text{C COOH} \end{array}$  will have both the carboxyls on the same side;

(2), that the acid in which both the carboxyls are on the same side will be the less stable. Moreover, (3), this acid only can

have an anhydride,  $\begin{array}{c} \text{HCCO} \\ || \\ \text{HCCO} \end{array} > \text{O}$ . The facts are in accord with

these demands of the theory; it is the same acid which is formed in (1), which is the less stable (2), and which has the anhydride

(3); in every case it is maleïc acid<sup>1</sup>  $\begin{array}{c} \text{HC COOH} \\ || \\ \text{HC COOH} \end{array}$ . Further, it is

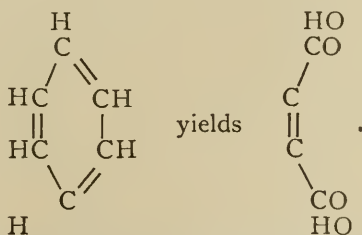
fumaric acid,  $\begin{array}{c} \text{HC COOH} \\ || \\ \text{COOH CH} \end{array}$ , that is formed by the splitting off of water from malic acid at 150°, because the favored configuration of malic

acid is  $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{C} \\ | \\ \text{OH}-\text{C}-\text{H} \\ | \\ \text{COOH} \end{array}$ . But it is maleïc acid that is formed by

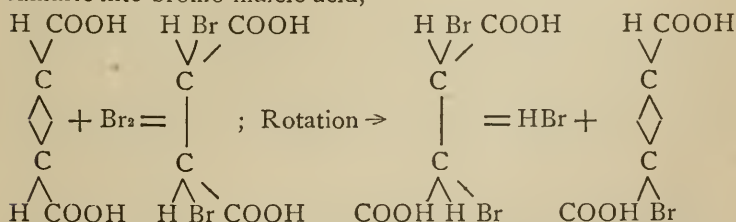
heating malic anhydride which can have only the configuration

$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{CO} \\ | \\ \text{C} \\ | \\ \text{OH}-\text{C}-\text{CO} \\ | \\ \text{H} \end{array} \text{O}$ . In the slow oxidation of benzene it is—as

the formulæ demand—maleïc acid which is formed:

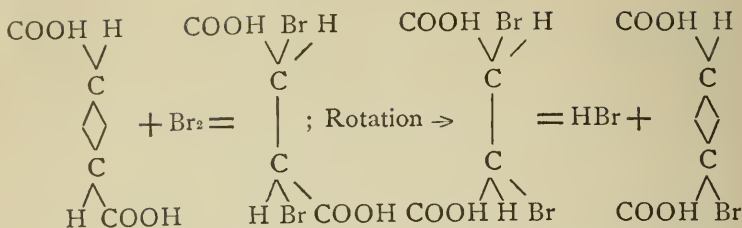


Further, the addition of bromine and subsequent removal of hydrobromic acid converts maleïc into bromo-fumaric acid, and fumaric into bromo-maleïc acid,



<sup>1</sup> Bandrowski found dibromo-fumaric acid to be formed by addition of bromine to  $\begin{array}{c} \text{C COOH} \\ || \\ \text{C COOH} \end{array}$ ; but Wislicenus showed that this was a secondary product, dibromo-maleïc acid being first formed.





These transformations can be properly represented only by models (solid formulæ); the formulæ given must be imagined solid.

In substances of the maleïc type (Fig. 18), like radicles have positions symmetrical with regard to a plane passing through the common edge at right angles to lines joining *aa* and *bb*. These substances are therefore called plane-symmetrical. Similarly, substances of the fumaric type (Fig. 19) are called center-symmetrical; or we may call them axis-symmetrical; the line of contact being the axis of symmetry.<sup>1</sup>

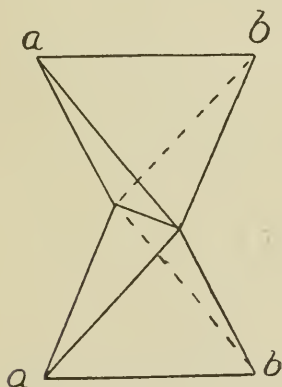


FIG. 18.

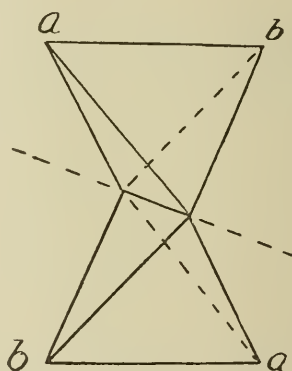


FIG. 19.

The stereochemical explanation of the isomerism of fumaric and maleïc acids has met with objections on the part of Michael<sup>2</sup> and of Anschütz,<sup>3</sup> "among which," says Victor Meyer,<sup>4</sup> "one may indeed be considered serious." Wislicenus had explained the ready transformation of maleïc into fumaric acid in the presence of hydrobromic acid, hydrochloric acid, etc., by the hypothesis

<sup>1</sup> In Wislicenus' treatise the axis of symmetry is incorrectly represented as in Fig. 20. The term center-symmetrical is preferred in the second edition.

<sup>2</sup> J. prakt. Chem. (2) 38, 21.

<sup>3</sup> Ann. Chem. (Liebig) 254, 168. Compare also Fittig; Ibid. 259, 1.

<sup>4</sup> Ber. d. chem. Ges. 23, 586.

that an addition-product was formed, that the now singly-linked carbon-atoms rotated until the most stable configuration was reached, and that then the added atoms again split off, leaving the more stable acid.

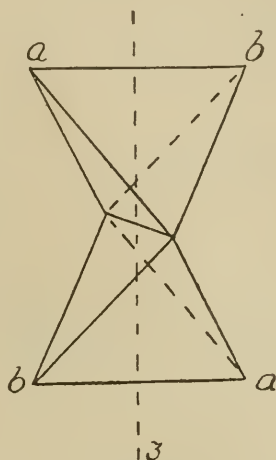


FIG. 20.

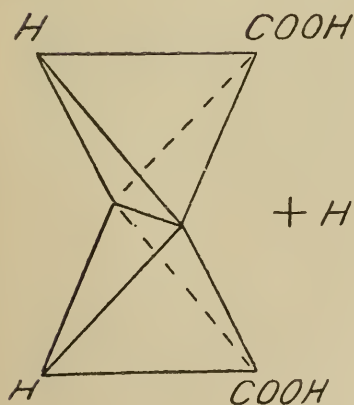


FIG. 21.

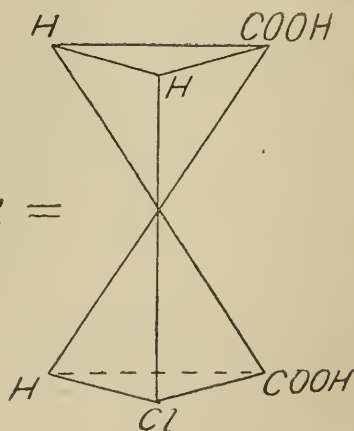


FIG. 22.

It was objected that only on boiling does the addition-product chlor-succinic acid give up hydrochloric acid and yield fumaric acid; whereas the transformation in question takes place at  $10^{\circ}$ . Whereon Victor Meyer remarks: "Wislicenus has not

to my knowledge been able to dispose of this objection in a satisfactory way." The explanation given by Van't Hoff<sup>1</sup> was, however, never open to this objection. The transformation involves

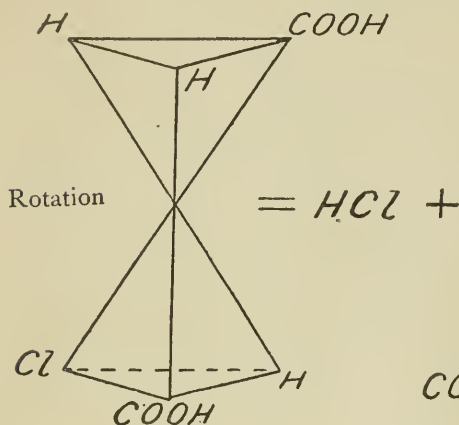


FIG. 23.

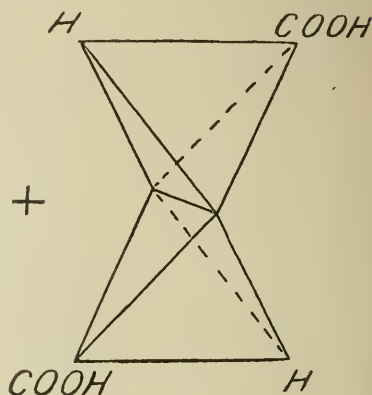
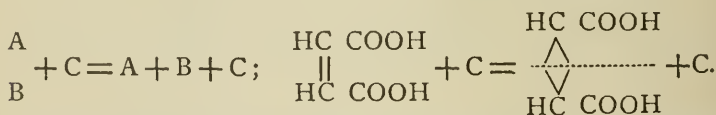
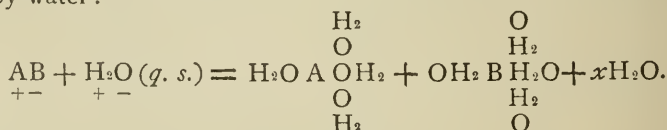


FIG. 24.

separation and then rotation of the four linked tetrahedron-corners. Now, addition also involves, as a necessary preliminary, separation of one pair of linked corners; but the symmetry of the maleïc acid molecule will cause both sides of it to be acted on alike; therefore *both* pairs of linked corners will be separated. So that before any addition has taken place the tetrahedron-corners will be on the way to their new positions.<sup>2</sup> This theory reminds us of the experiments of Morse and White,<sup>3</sup> showing that the dissociation of a compound AB is favored by the presence of a substance C capable of combining with A or B.



The explanation of both cases of dissociation is perhaps analogous to that given by Ciamician<sup>4</sup> for the dissociation of electrolytes by water:



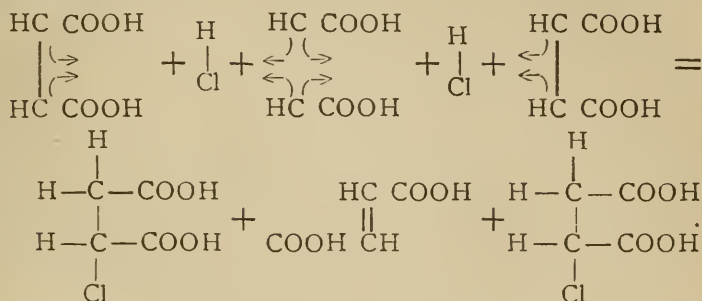
<sup>1</sup> L. c. p. 90.

<sup>2</sup> Bischoff also is of opinion that no actual addition takes place, and has supported this opinion by experiments.—Ber. d. chem. Ges. **23**, 1925.

<sup>3</sup> This Journal **11**, 260.

<sup>4</sup> Ztschr. phys. Chem. **6**, 403.

"Failure of C to maintain the dissociated condition of A and B might result from a lessening of its relative quantity." (Morse and White.) *E. g.*



Thus the formation of an addition-product would favor the transformation of molecules not directly affected by the addition. But addition does not seem to be essential. The attraction of a substance capable of forming addition-products may suffice to

destroy the equilibrium of the less stable molecule  $\begin{array}{c} \text{HCCOOH} \\ \parallel \\ \text{HCCOOH} \end{array}$  and yet not suffice to prevent the formation of the more stable molecule  $\begin{array}{c} \text{HCCOOH}^1 \\ \parallel \\ \text{COOHCH} \end{array}$ . This, the explanation of Van't Hoff,

accounts for the transformation effected by traces of bromine or iodine, and seemed to be the most generally applicable hypothesis. But the researches of Skraup<sup>2</sup> conducted especially with a view to determine the conditions necessary for the conversion of maleic to fumaric acid, show that the conversion takes place not only when there is no addition, but when there is probably no tendency to the formation of addition-products. Skraup is convinced that conversion is the catalytic accompaniment of certain chemical actions; that oscillations<sup>3</sup> of the binding-points in the direction of conversion characterise the double-bond, and that these may be reinforced by neighboring oscillations of the proper pitch produced by chemical action between other bodies, until, the upper and lower halves of the molecule each swinging through 90° in opposite directions, an interchange of binding-points takes place.

This discussion illustrates the elasticity of stereochemical theory with regard to these transformations—an elasticity which

<sup>1</sup> Compare Grubler's analogy quoted by Bischoff (*l. c.*): "A piece of iron alters the direction of a magnetic needle from afar, but holds the needle fast only when in immediate contact with it."

<sup>2</sup> Monatsh. Chem. 12, 107.

<sup>3</sup> Compare *ante* p. 576. The planes in which these oscillations take place are at right angles to the plane of the oscillations there described.

makes it impossible to crush the theory by the pressure of facts bearing on isolated points, but indicates at the same time a vagueness which only future experiments can diminish. Meanwhile the contest' between Wislicenus and his opponents continues.

ARNOLD EILOART.

[To be continued.]

## NOTE.

### *The Preservation of the Alkali Metals.*

M. Rosenfeld<sup>2</sup> describes a method for removing the crusts of hydroxide from metallic sodium, potassium and lithium, and for keeping these metals bright. Bring the metal into a mixture of one part of amyl alcohol and three parts of petroleum, and with a rag rub it under the liquid till it is silvery white. Put it for a few minutes in petroleum containing 5 per cent. of amyl alcohol; then wash it thoroughly with pure petroleum. Finally, preserve it under petroleum to which from 0.5 to 1 per cent. of amyl alcohol has been added. The metal remains bright under these conditions for a long time, but finally becomes covered with a coating of amylate, which is, however, easily removed by rubbing with filter-paper.

E. R.

<sup>1</sup> Wislicenus: Ann. Chem. (Liebig) **246**, 53; compare Fittig's reply; Ibid. **259**, 1. Blank: Ibid. **248**, 1. Wislicenus: Ibid. **248**, 281. Compare Michael's reply: J. prakt. Chem. [2] **40**, 29. Wislicenus: Ann. Chem. (Liebig) **250**, 224. Compare the reply of Favorsky and Debout: J. prakt. Chem. [2] **42**, 149.

<sup>2</sup> Ber. d. chem. Ges. **24**, 1658.



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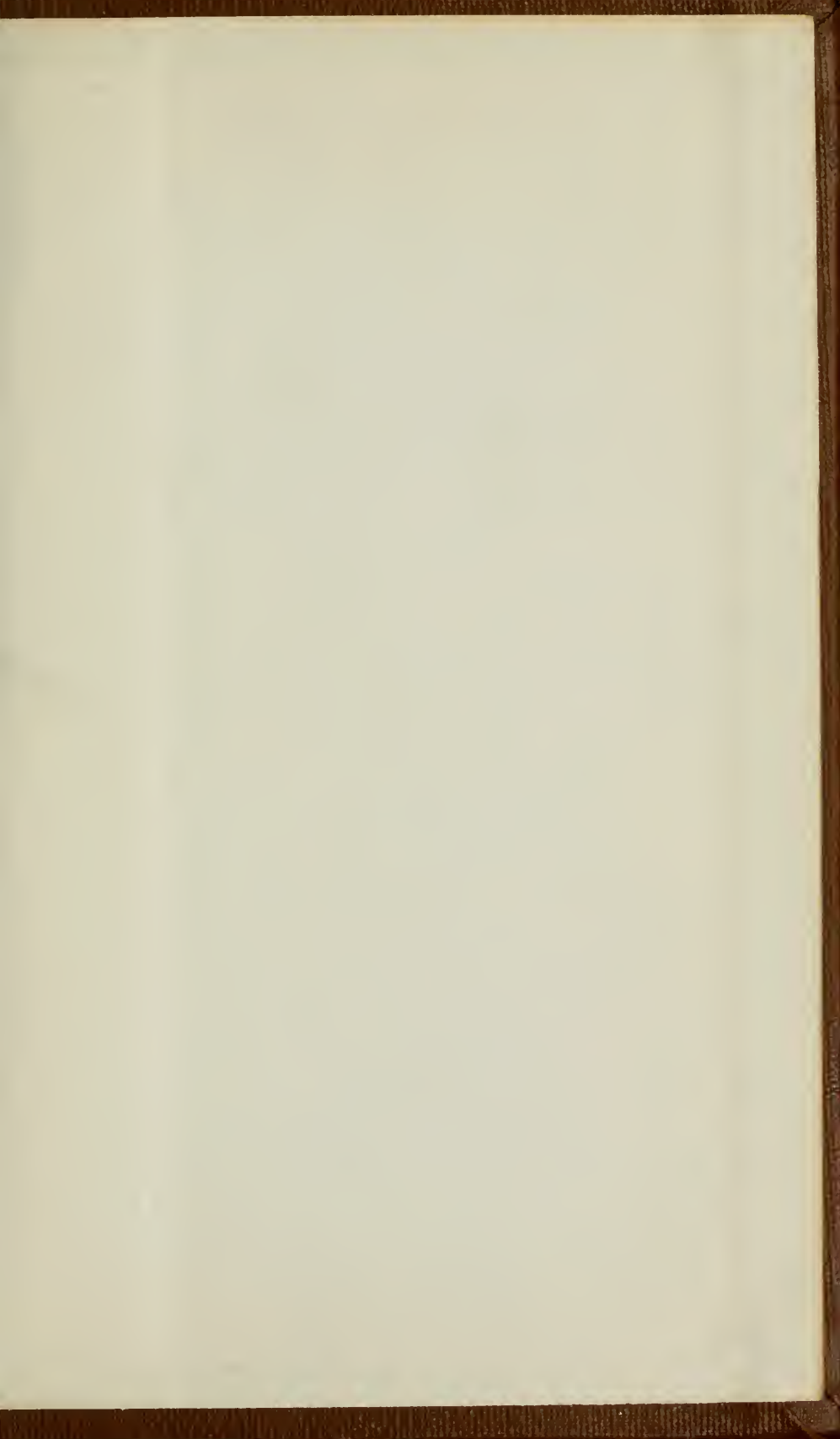














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